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Engineering Materials for Very High Temperatures
An ONRL Workshop

Louis Cartz

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<p>The limitations of present-day materials at very high temperatures are reviewed; silicon nitride based ceramics, silicon carbide, carbon materials. Near-term and long-term studies are described to improve the performance at temperatures above 1400°C of monolithic ceramics, composites, and ceramic coatings. The full texts of the papers given at the workshop are included. Keywords: Microstructure, Strength Mechanics</p> <p style="text-align: right;">(AW)</p>			
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ENGINEERING MATERIALS FOR VERY HIGH TEMPERATURES – AN ONRL WORKSHOP

Abstract. Using the gas turbine engine as an example, the limitations of present-day materials were pointed out and future requirements with significantly higher temperature capability were indicated. The properties demanded are high strength and toughness, and creep and oxidation resistance at high temperature, but cost-effective processing and reliability are equally important.

Among the ceramic materials discussed, silicon nitride-based ceramics allow use at up to about 1250°C, which might be extended up to 1400°C. Silicon carbide has a better performance at high temperatures but suffers at present from a low fracture toughness which needs to be improved. Carbon-containing materials could be used at temperatures of perhaps 2000°C, but for use of these materials in air, protection against oxidation needs to be provided, which is not an easy problem to solve. The same applies to the protective coatings on refractory metals, which require a better understanding of their adhesion and diffusion properties. Among new materials to be studied, the silicides and borides were suggested.

The fracture toughness of ceramic materials might be increased by the incorporation of fibers and whiskers; presently this approach is limited by the availability of suitable fibers and whiskers – current composite materials do not display better fracture toughness properties at high temperatures than monolithic ceramics. However, there are signs of improvement of this situation.

The mechanism of sintering aids which do not form liquids, as used in the sintering of silicon carbide, requires elucidation.

This report makes recommendations for "near-term" and "longer term" studies. Collaboration between suppliers and users is essential, with the latter defining quantitatively their requirements. A coordinated program aimed at the manufacture of components, in which universities and research institutes play their part – such as is sponsored by the government of West Germany – was suggested.

Introduction

This workshop, "Engineering Materials for Very High Temperatures," sponsored and organized by ONRL, was held at the University of Warwick, Coventry, UK. It was part of a conference, "New Materials and their Applications," which was arranged by the Institute of Physics (IOP). General chairman of the workshop was P. Popper, Editor, *High Technology Ceramics*, UK.

The objectives of the workshop were to:

- Discuss research studies likely to lead to engineering materials useful at high temperatures
- Formulate recommendations or conclusions concerning high-temperature engineering materials research.

Dr. Cartz was the Liaison Scientist for Materials Science in Europe and the Middle East for the Office of Naval Research's London Branch Office. He has now returned to Marquette University, College of Engineering, Milwaukee, Wisconsin, where he is a Professor of Materials Science.

The workshop consisted of four sessions. At the first two sessions, eight papers were presented of the different aspects of high-temperature materials:

- Limitations at High Temperatures of Present Day Materials, by G.W. Meetham (Rolls-Royce, UK)
- A Review of Engineering Ceramics in West Germany, by P. Popper (UK)
- The Shaping of Structural Engineering Ceramics, by R. Carlsson (Silicate Research Institute, Sweden)
- High-Temperature Ceramics for Energy Conversion Applications, by R. Metselaar (Eindhoven University of Technology, the Netherlands)
- The Microstructure of High-Temperature Engineering Ceramics, by M. Lewis (University of Warwick, UK)
- Time-Temperature Dependence of High-Performance Ceramics, by R. Katz (Army Materials Technical Laboratory, Watertown, US)
- Surface Modification and Coatings, by M. Grilhé (Université de Poitiers, France)
- Ceramic-Ceramic Composites for Use at High Temperatures, by J. Jamet (ONERA, France).

The talks were intended to proceed from present-day materials in the earlier lectures, to future possibilities in the later lectures. Copies of these papers are given in Appendix C of this report.

Subsequent to the two session of papers, there were two discussion sessions. The first session was held as part of the overall IOP meeting, so that a relatively large audience was present. The discussion session was led by Dr. J.D. Birchall (affiliations of participants are listed in Appendix A).

A second discussion, held later in the evening, was limited to a small number of participants—about 30. These consisted of the lecturers; the chairmen of the sessions, Dr. P. Popper, Professor P. Boch, Dr. D. Thompson, Dr. J.D. Birchall, and Dr. L. Cartz; and special invitees, including Sir P.B. Hirsch, Professor A. Kelly, Dr. G. Dunlop, Dr. S. Burnay, and Professor C.H.L. Goodman.

Discussion

The comments raised during the discussion periods are summarized here. These followed on from a review by Birchall of the eight papers presented during the two sessions. Birchall commented that it is necessary to understand the sintering mechanisms of ceramics, for which fundamental studies are required.

G.W. Meetham, as a user of materials, was highly concerned with reliability, where defect tolerance is essential. He gave the example of the growth of crack length (L) with the number of cycles of use (N_c). Increasing the toughness level may not alter N_c appreciably, whereas decreasing the rate of crack propagation is likely to permit a larger N_c for the same fracture toughness level. Meetham said that achieving slower crack growth may be more advantageous than increasing fracture toughness.

Dr. J. Jamet described how the user can only be interested in systems which perform as required, and that cheaper methods of processing of systems need to be developed if such systems are to be used in practice.

Dr. R. Carlsson was concerned with ceramic forming processes. Slip casting methods are excellent though not useful in the presence of long fibers. He thought that it should not be necessary to use HIP except possibly when using fiber/whisker reinforcement. Health hazards with whisker processes can be overcome and do not represent a serious difficulty.

Professor Kelly discussed the development of techniques such as those used in macrodefect-free cement. Another technique, the Lanxide process, uses metal matrices which are then oxidized, though at present, it is difficult to take the reaction to completion. All other possible high-temperature systems should be considered, such as, among others, BN, MoSi₂, Pt with Al₂O₃, and WC with a high m.p. metal.

Dr. Thompson pointed out that there is a lot of potential in composite materials and in the modeling of their

microstructures, though there are still serious problems of corrosion and oxidation at the highest temperatures.

Sir Peter Hirsch discussed the brittle nature of ceramics and raised questions concerning the behavior of dislocations in ceramic materials, and as to whether it would be possible to introduce dislocations in the processing stage to act as crack-blunting entities. Dr. M. Lewis replied that the mobility of dislocations in ceramics such as Si₃N₄ and SiC is inadequate, at normal service temperatures, to effect crack blunting. Moreover, crystal anisotropy in many ceramics is such that the limited number of slip-systems may cause nucleation of intergranular cracking. Lewis emphasized that at high temperatures and modest stress levels monolithic ceramics have an important role: composite ceramics are not yet competitive in relation to structural stability at high temperatures and sensitivity to oxidizing environments. There is also little available knowledge of their time-dependent deformation and fracture behavior.

Conclusions

The following conclusions and recommendations are based on those of the panel-discussion at the time of the meeting, modified and reviewed by the subsequent special review meeting of Drs. Lewis, Thompson, Popper, and Cartz.

In the temperature interval 1000-2000°C, ceramics have to be considered as major contenders for applications under stress, especially in oxidizing conditions. It is recognized that this is a wide range of property requirements for the different uses of ceramics at high temperatures. The structural state of the ceramics may be broadly classified:

1. Monolithic ceramics (with mono- or multi-phase microstructures)
2. Composite ceramics (with nonsintering additives)
 - dispersion/whisker-toughened matrix
 - "reinforcement" with semicontinuous fibers of high volume fraction
3. Ceramic coatings (as thermal or corrosion barriers on metallic or ceramic substrates).

Table I summarizes current research on the properties of high-quality materials of nitride and carbide ceramics. In the table, T_{max} is the maximum temperature of use, determined mainly by oxidation performance; σ_{RT} is the room-temperature tensile strength; K_{IC} is the critical fracture toughness.

TABLE 1. Current Data on Nitride and Carbide Ceramics

	T_{max} (°C)	σ_{RT} (MPa)	K_{IC} (MPa ^{1/2})
Si ₃ N ₄	1450	1000	6
Sialon	1350	1000	8
SiC	1650	500	4

Current ceramics based on Si_3N_4 and of sialons have probably the best balance of strength-toughness at temperatures up to 1300°C . Monolithic SiC is brittle but has better high-temperature behavior than the nitrides. Composite ceramics are currently dominated by oxidation and fabrication problems, though potentially they offer the best combination of strength/toughness above 1500°C . However, better protective coatings against oxidation are required and the properties may even then be critically time-dependent.

There is a modest understanding of microstructure-property relationships in high-temperature creep, fracture, and oxidation of monolithic ceramics. Monophase ceramics, exemplified by solid-state-sintered SiC , have good time-dependent properties to 1600°C but have microstructures with poor fracture toughness ($5 \text{ MPam}^{0.5}$). Some improvement in fracture toughness ($6\text{--}8 \text{ MPam}^{0.5}$) is attainable in liquid-phase-sintered Si_3N_4 and sialon ceramics, which retain good creep, creep-rupture, and oxidation resistance to 1300°C provided that the liquid residues are fully crystallized. Instability in oxidizing conditions above 1350°C may be improved by reducing the residual phase content and using hot isostatic pressing (HIP) fabrication, but fracture toughness is normally impaired.

Composites have a potential for removing one of the most important engineering design limits of monolithics—that of microscopic critical flaw sizes associated with low fracture toughness. Useful increments in toughness ($10\text{--}15 \text{ MPam}^{0.5}$) are attainable by dispersion of whiskers (10–30 volume percent) in various matrices, retaining conventional fabrication procedures but normally requiring pressurized sintering. Fibrous composites are based on the totally different concept of load-transfer to component "overload" situation. Although they exhibit impressive unidirectional fracture properties, there are significant problems in high-temperature stability of non-stoichiometric fibers (such as Nicalon- SiC), in fabrication of refractory matrices with nonreactive fiber/matrix interfaces, and in the forming of three-dimensional woven-fiber component shapes capable of retaining a large fraction of the unidirectional property. Oxidation-induced microstructural instability is also a problem, especially for C-fibers, but there has been some progress in the use of protective coatings. High-temperature deformation and creep-fracture of both fibrous and whisker composites remains a relatively unexplored field.

The more complex, difficult, and hence expensive fabrication processes for high-temperature monolithic ceramics—and especially for composites—must be weighed against the increment in high-temperature performance over the lower temperature metallics. Of particular interest here is the novel formation of monolithic and composite ceramic shapes by the "Lanxide" process in which a liquid metal matrix is converted, for example, to an oxide ceramic. Whereas the incomplete metallic conversion is beneficial for fracture toughness, it clearly

presents problems in relation to high-temperature operation above the liquidus for the metallic residue.

Recommendations

Two groups of studies need to be considered: studies which lead to near-term optimization of useful materials and longer-term studies aimed at the understanding and development of those more esoteric composite structures which have a much greater potential for property gain.

Examples of such studies and their aims are:

Near-term

- Increasing the temperature ceiling of Si_3N_4 -based monolithic ceramics to at least 1400°C in oxidizing conditions, using stable crystalline sintering residues and HIP processing.
- Improving the fracture toughness and strength of SiC -based ceramics, formed by solid-state sintering, by particulate or whisker dispersions, while retaining the good creep-rupture and oxidation resistance of the sintered matrix.
- Further development of SiC or C-based fibrous composites with respect to stability at temperatures $> 1200^\circ\text{C}$, especially in oxidizing conditions (e.g., by coatings for C-C composites and the use of the newly emerging stoichiometric SiC fibers).
- Development of coatings on metals (e.g., superalloys) of refractory silicates (celsian, for example) of matched thermal expansion behavior, made by the glass-ceramic route, replacing existing oxide coatings.

Longer Term

- The development of a range of new particulate dispersants, with controlled morphological anisotropy, and chemical compatibility with Si_3N_4 - and SiC -based matrices, designed to extend the principle of "whisker-toughening."
- Further development of high-stability fibers, such as stoichiometric SiC , and of nonreactive interfaces with refractory matrices. This may be achieved by coatings or by using lower temperature fabrication such as the "sol-gel" route for oxides, or "reaction-bonding" for Si_3N_4 . The present-day limited choice of fibers is a severe handicap; it would be very useful to have fibers of materials such as BN, BC, and AlN.
- Development of shaping/fabrication procedures, especially for fibrous composites, with an emphasis on property targets for specific component application (see comments from Meetham and Dunlop—Appendix B).
- Develop a better understanding of the basic mechanisms involved in sintering, both of monolithics and composite matrices, and of high-temperature deformation and fracture. In "dispersed-phase" composites, the relative contributions of different toughening mechanisms should be investigated.

- Develop an understanding of coating cohesion and substrate interdiffusion.
- Examine the properties of other high-temperature materials, such as those based on borides, silicides, and carbides.
- Develop methods of flaw detection in ceramics to permit the study of the smallest flaws under stress and environment, as well as to obtain more consistent properties in ceramic materials.
- There is a lack of data of the mechanical properties of ceramics above 1400°C, and data is required certainly up to 1600°C. Measurements techniques to acquire this data must be developed.

Acknowledgements

The Institute of Physics (IOP), UK, was responsible for organizing the 4-day conference on "New Materials

and their Applications," of which the ONRL Workshop represented the sessions of the first day. Considerable help was provided by the meetings office of IOP in the setting up of the meeting. Dr. S. Burnay was secretary of the 4-day conference, and provided considerable help for the workshop, in particular making notes of the discussion periods.

The proceedings of the meeting are published by IOP as part of their conference series (*Institute of Physics Conference Series 89: New Materials and Their Applications*, Bristol, 1988), and this report is published in agreement with them. The papers of the ONRL workshop will appear, possibly in a modified form, in the journal *High Technology Ceramics*.

The recommendations have benefited from further discussions and suggestions from Drs. Lewis, Thompson, and Popper at a discussion meeting held in March 1988.

Appendix A

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Appendix B

WRITTEN COMMENTS

These comments were prepared by Birchall, Meetham, Thompson, and Dunlop, subsequent to the discussions.

J.D.Birchall:

Following the presentation of individual papers, the speakers, joined by Professor Sir Peter Hirsch, assembled as a panel for a general discussion of engineering materials for high temperature. The various lectures had explored the limitation of existing materials (superalloys) and outlined the properties demanded of new materials – high strength and toughness, resistance to creep at high temperature and to oxidation and acceptable reliability – a Weibull modulus greater than 20.

The panel was faced with three fundamental questions: what materials? how to fabricate? and how to test? Because of the difficulty of detecting flaws a few microns in size in a component, it was felt that reliability would need to be "built-in" to the fabrication process with tight control of microstructure-voids, grain size, grain boundary, composition, etc. For ceramics made by powder routes this would demand particular powder characteristics of size, shape and purity and this raised the issue of availability. Even given an optimized powder the forming process would dictate final properties, and there was felt to be a need for matching the powder and forming process to obtain "packaged reliability."

There was some discussion of "ductile ceramics" and dislocation mobility in non-oxides such as silicon carbide, but the emphasis was on fiber-reinforcement. The availability of appropriate fibers is a problem, as is the fabrication of the composite structure. Fibers inhibit pressureless sintering, forcing the use of HIPping or chemical vapor infiltration (CVI), both of which are expensive processes for the fabrication of large components.

The role of sintering aids – for example, boron in SiC – was discussed with the conclusion that too little was known of mechanisms at a fundamental level. This is particularly true of sintering aids which do not form a liquid, and more research is needed.

The lectures concentrated on SiC and Si₃N₄ and little was said of other carbides and nitrides (except as surface coatings) or of borides and silicides and the prospects of mixed systems showing advantages at high temperature. There was felt to be a shortage of basic data for such materials, especially as regards high-temperature properties. Carbon and carbon/carbon composites remain attractive materials, good for 2000°C in the absence of oxygen, and better means for increasing oxidation resistance is worthy of continued research.

G.W.Meetham:

The subject chosen – high-temperature materials – is most appropriate at this time. The need for materials with higher temperature capability has never been greater.

The balance of papers was good, with most major relevant material systems being covered. One possibility for future workshops could be a slightly increased user involvement – possibly involving, say, the two major potential user industries. I think that this is important because the commercial development of new nonmetallic materials will undoubtedly require multi-industry usage.

The major technical messages that came out of the workshop were:

1. A clear, quantified definition of user requirements is crucial.

2. Detailed collaboration is necessary between user and potential supplier to define work programs to meet the requirements, or to meet mutually agreed modifications to the initial user requirements. University involvement is crucial.

3. The need for defect tolerance in new nonmetallic materials is essential to ensure component reliability in engineering applications. (The precise definition of what constitutes defect tolerance and how it can be achieved should form an integral part of the collaboration referred to in 2.)

4. The other major requirement is a detailed understanding of material behavior. The workshop confirmed encouraging evidence that this understanding is being developed.

It is for debate as to whether the format of the workshop could be improved. Audience participation was almost nonexistent. I feel that more extensive discussion could have been achieved in a different environment with around a dozen experts from various disciplines.

D.Thompson:

Current engineering materials for high-temperature (> 1000°C) applications include monolithic ceramics based on silicon nitride (sialons) or silicon carbide, composite materials (especially those with carbon and silicon carbide fiber reinforcement) and also some oxides. Current research areas are concerned with:

- Improving the high-temperature capability of existing materials
- Improving the mechanical performance – especially fracture toughness

- Improving fabrications procedures to make reproducible, fully dense products which exhibit predicted behavior
- Developing new materials.

Existing silicon nitride/sialon-based materials can currently be used up to 1300°C, but there is scope for further research into heat-treatment procedures and minimum additive levels to increase this figure by at least 100°C. Silicon carbide ceramics exhibit a lower fracture toughness, and this must be increased for these materials to realize their full potential. SiC-SiC composites are exciting materials for high-temperature use, but improved processing procedures are necessary to produce high-strength products which retain the predicted high fracture toughness.

High-temperature oxide ceramics featured very little in the conference program, but these materials are also contenders for high-temperature use if problems such as control of grain growth and satisfactory mechanical performance can be obtained. Reinforcement may be necessary to achieve this.

Some discussion ensued on further development of boron compounds. Currently, boron carbide is being developed, boron nitride (cubic and graphite) has its own specific range of applications, and several metal borides (e.g., TiB₂) are being used, especially in composite materials. This range of compounds is by no means exhaustive and further research into these materials may prove very fruitful.

Current developments in the production of pure powders of well-defined microstructure and surface area are encouraging. However, the sintering process is still relatively poorly understood and optimization of all the variables concerned is often achieved on a crude empirical level in the absence of a more detailed theoretical un-

derstanding. Further developments here and especially along lines which can predict minimum flaw size in terms of powder particle size distribution and other sintering variables would be most useful even though such advances are probably a long-term achievement.

Gordon Dunlop:

The limitations of engineering materials at high temperatures were clearly pointed out in the paper by G.W. Meetham. However, subsequent papers showed that processing technology with the abilities of manipulating microstructure exist in order to tailor-make materials which can fit moderate requirements, albeit requirements which are considerably less demanding than those specified by G.W. Meetham.

In order to make use of this know-how and extend it in those areas where it is deficient, I would like to suggest the creation of coordinated R&D programs aimed at the manufacture of components which fulfill reasonable design requirements. One of the problems in such a program is identifying suitable components which provide the right scientific/technical challenge and which have reasonable prospects of being successfully developed and marketed in a set time period. Such a program should be able to test the skills and provide sufficient scientific challenge along the chain from initial design through selection of raw materials to completion of finished product. At the same time the project should have a reasonable chance of successful completion in the time scale allotted.

I believe that well-designed programs such as these can lead to significant advances in the materials science of engineering ceramics as well as to important technical results.

Appendix C

Papers Presented at the Workshop

Microstructure of High-Temperature Ceramics	M.H. Lewis	C-2
Ceramic-Ceramic Composites for Use at High Temperature	J.F. Jamet	C-13
Development of Composite High-Temperature Materials for Future Energy Conversion Applications	R. Metselaar and L.R. Wolff	C-27
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Microstructure of High-Temperature Ceramics

M.H. Lewis

Centre for Advanced Materials Technology, University of Warwick, U.K.

ABSTRACT: After more than a decade of intense activity in development of monolithic ceramics they have limited application as engineering components at elevated temperatures. There is now a good understanding of deformation and fracture mechanisms and hence of the principles for design of 'ideal' microstructures. This is rarely achievable in practice due to the conflicting requirement for ease of fabrication or the inability to 'tailor' the geometrical or chemical characteristics of microstructure via. natural reactions during sintering. The artificially-produced microstructure of the ceramic composite is an alternative. High temperature properties of these varied microstructures are surveyed.

1. HISTORICAL PERSPECTIVE

The 1970's are remembered in the ceramic world as an era of great promise for widespread application of the 'Si-based' ceramics (Si_3N_4 and SiC) as engineering components. In the 1980's we have observed the gradual introduction of ceramics as non-strategic components at modest temperatures but there has been little impact in the high stress/high temperature regime with consequent influence on energy-efficiency. Thus the various 'engine' programmes have not achieved a significant commercial development status. There are various contributions to this problem; (i) the difficulty in fabricating complex component shapes economically, with properties which replicate those of laboratory-scale test-specimens, (ii) the restrictions imposed on engineering design and failure-prediction by low fracture toughness materials.

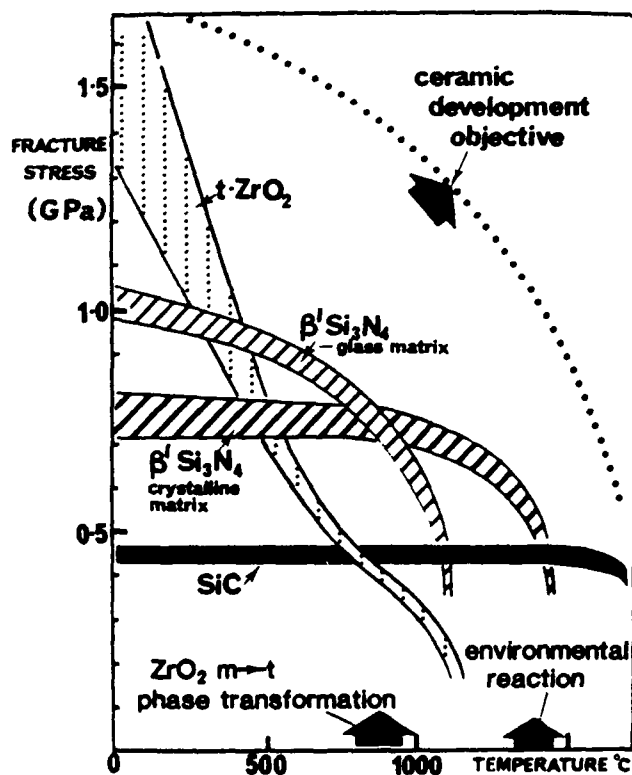
Structural ceramic development has reached a critical phase. There is a modest understanding of deformation and fracture mechanisms over a range of temperature and hence of the requirements for 'ideal' microstructures, tailored for the varied stresses, temperatures and environments in service. However, it is clear that these optimal microstructures are rarely produced via. 'natural' reactions and transformations which occur during conventional ceramic fabrication procedures.

A simplistic comparison of time - independent strength (MOR) for a range of structural ceramics developed in the 1970's (Fig 1.) demonstrates the compromise between low and high-temperature properties. Silicon carbide ceramics may be solid-state sintered at ultra high temperatures resulting in an absence of grain boundary residual phases and hence superior high-temperature strength. However, this is inferior to the Si_3N_4 -based ceramics at lower temperatures, due principally to lower fracture

toughness (K_{IC}) and higher porosity. The nitrides require liquid - assisted sintering at modest temperatures with inevitable intergranular residues and high temperature property impairment. Zirconia (ZrO_2) based ceramics are an important development of the late 1970's, resulting in a quantum leap in low temperature strength and fracture toughness with an indication that 'damage - tolerant' behaviour, characteristic of metallics, is attainable. The achievement of these superior properties requires critical microstructural parameters. They have an important place as low-temperature engineering materials but, because the toughening effect is based on a martensitic phase- transformation there is a catastrophic loss of strength well below the transformation temperature ($\sim 1000^\circ C$). Also the relatively high thermal expansion and low thermal conductivity for ZrO_2 presents a thermal shock problem even in conditions where microstructural stability is retained on thermal cycling. Hence the high covalency Si -based ceramics remain the principal contenders for applications above $1000^\circ C$. Bearing in mind the long development period for these ceramics it is now probable that to design and fabricate a ceramic which extends to the high temperature/high stress frontier (Fig. 1) we must look to microstructures which are artificially generated, i.e. ceramic composites.

Fig.1.

A comparison of strength-temperature relationships for various monolithic ceramics.



2. IDEAL MICROSTRUCTURES

To identify microstructural parameters of importance for the high temperature/high stress regime it is convenient to refer to some of the established mechanisms for deformation and fracture. Fig. 2 is a survey of microstructural variables within a stressed ceramic element containing a sub-critical crack. Potential toughening mechanisms are:

(i) 'Microcracking' at grain or particle interfaces within the stress- field of a sub-critical crack, shielding the latter from the influence of applied stress [Faber and Evans 1983]. The origin of this effect may be anisotropy

in thermal expansion of grains in a monophase ceramic or differential expansion between dispersed phase particles and matrix in a multiphase ceramic. A restrictive feature of this toughening mechanism is the need for a critical range of particle or grain size above which a general microcracking occurs, in the absence of the crack-tip field, or below which microcracking may not be initiated by the sub-critical crack. The implication is that of careful control of phase-combination and thermal-treatment in processing. It is unlikely to be a significant mechanism at high temperatures due to loss of the differential thermal property coupled with a greater probability for relaxation of residual microscopic stresses via. plasticity or diffusion.

(ii) 'Crack deflection' toughening is applicable to a wide temperature range and stems from the reduced crack-tip stress intensity when the crack deviates from the plane normal to the axis of applied stress and from repeated bifurcation of the sub-critical crack. Analysis of the deflection mechanism [Faber and Evans 1984] shows that a twist deflection is most effective and that the obvious effect of anisotropy in grain or particle morphology (defined by l/w in Fig.2) saturates at values of ~ 10 . There is a similar relation for volume fraction (of particles) such that the main increment is already present at ~ 10 vol% (Fig.2). Particle or grain size is not critical.

(iii) 'Crack-bridging' by anisotropic grains or second-phase particles in the wake of a sub-critical crack is also effective over a range of temperature. Like both of the above mechanisms it relies on the formation of a relatively weak grain or particle interface and, in this case, a critical ratio of particle fracture stress to interface shear stress (τ_i - Fig.2). Thus 'non reactive' or 'van der Waal' type interface cohesion is favoured, with τ_i dictated by sliding friction. Interface area and hence volume - fraction is an important parameter, expected to saturate near the 50% level. The scale

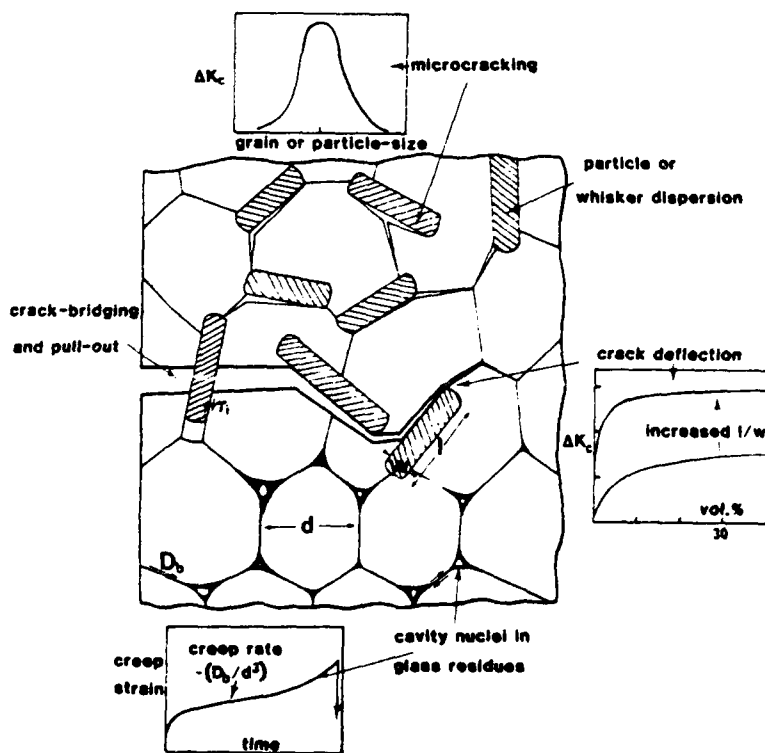


Fig. 2.

The relation between microstructural parameters and mechanisms for increasing fracture toughness, high temperature creep and creep-rupture resistance.

of microstructure (i.e. average separation of interfaces) is important in relation to natural flaw size such that sub-critical flaws may experience a 'rising-resistance' to propagation ('R-curve' behaviour).

The above factors relate to brittle crack propagation. At elevated temperatures time-dependent (creep) deformation and creep rupture are additional problems. In high covalency ceramics dislocation plasticity plays a negligible role by comparison with grain-boundary shear and the parallel, normally rate-controlling, mechanism of diffusional creep. A grain boundary diffusion (Coble) mechanism is normally dominant with strain rate, $\dot{\epsilon}$, proportional to D_b/d^3 (Fig.2), where D_b is the boundary diffusion coefficient and d the mean grain size. Large grain sizes are constrained by the inverse requirements of flaw-size limit and 'microcracking' or pull-out contributions to fracture-toughness. However, the normally small values of D_b for intercrystalline ceramic boundaries relieve this conflict. Creep-rates only become a significant problem when ceramic interfaces contain glassy phases which are normally the residues of liquid - assisted sintering. A simple energy balance argument shows that these liquid residues will concentrate in grain junction channels (Fig. 2) if the solid/solid interface energy γ_{ss} is less than $2\gamma_{sl}$, the solid/liquid interface energy [Raj 1981]. Thus the liquid residues assume a greater importance in creep rupture, acting as sites for easy cavity nucleation during grain boundary shear [Karunaratne and Lewis 1980]. Ideal creep and creep-rupture resistant microstructures must be totally crystalline and, additionally, retain a geometrical and chemical stability for the required component lifetime and service environment.

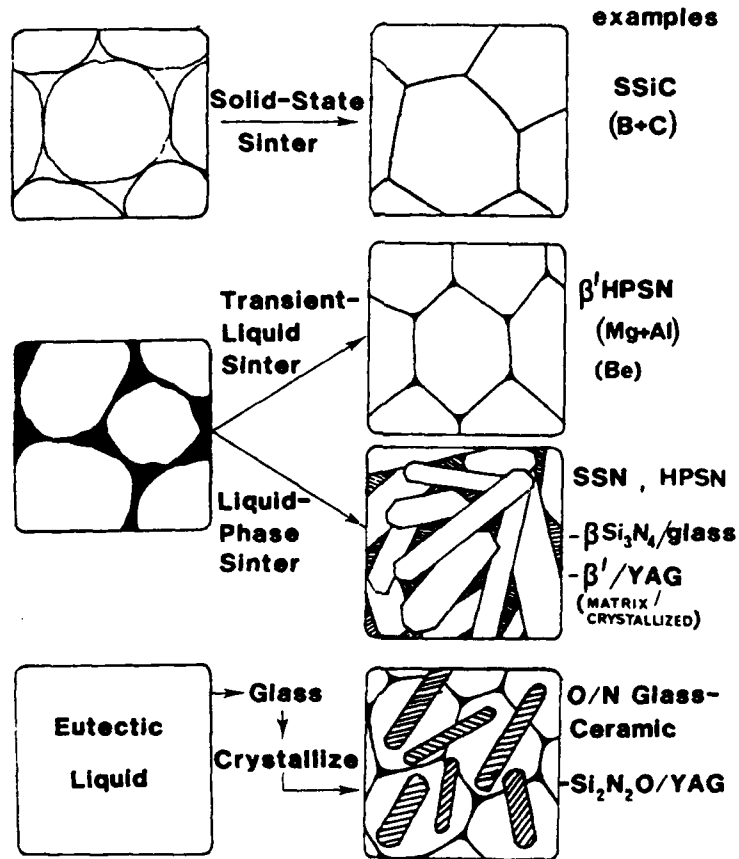
3. REAL MICROSTRUCTURES

A complete freedom in microstructural design is normally constrained by the fabrication process with a requirement for full densification using accessible temperatures, pressures and shaping procedures. There is an additional conflict if the ceramic properties have to be optimised for a wide range of application temperature.

Examples of monolithic ceramic microstructures produced via. different fabrication routes are shown schematically in Fig. 3 and in the electron micrographs of Fig. 4. The simplest microstructures are the monophasic ceramics formed by solid-state sintering, usually with added impurities to inhibit grain growth or to modify surface energy and reactivity, e.g. B+C to SiC. The polycrystalline structure is typical of that in metallic systems, with nearly isotropic grain morphology and non faceted interfaces characteristic of small variations in energy anisotropy.

Si_3N_4 based ceramics require liquid-phase assisted sintering; solid state diffusivity is too small for temperatures below the decomposition point which is much lower than for SiC. There are rare examples of 'transient' - liquid sintering in which the components of an oxynitride liquid are progressively removed with consequent formation of solid-solid grain boundaries in the final stage of sintering. Al and Be are the only elements which form extensive solid solutions in $\beta\text{Si}_3\text{N}_4$, when accompanied by oxygen. The formation of monophasic ceramics via. this route dictates that the liquid volume is small and hence full densification requires pressure-assisted sintering e.g. the hot-pressed Si-Al-O-N ceramics [Lewis et al 1977] which have grain morphologies similar to the solid state sintered SiC ceramics (Fig. 3 & 4).

MONOLITHIC CERAMIC MICROSTRUCTURES



COMPOSITE CERAMIC MICROSTRUCTURE

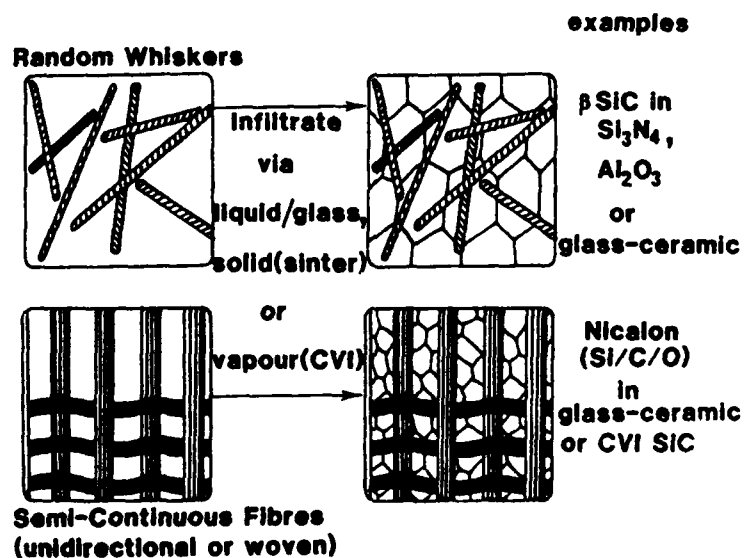


Fig. 3.

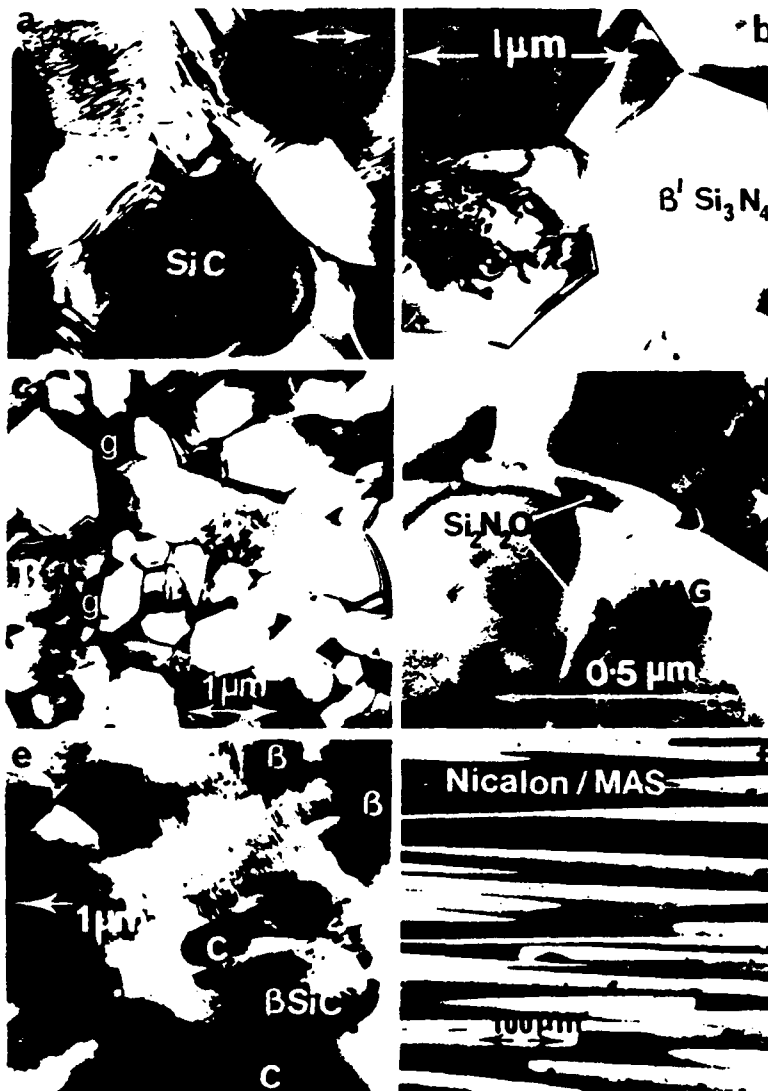
Examples of the different types of ceramic microstructure which may be developed under varied processing conditions

Pressureless sintering of Si_3N_4 -based ceramics normally requires 5-10 vol. % of a sintering liquid. This is generally of M-Si-O-N composition in close proximity to a silicate eutectic with liquidus in the 1300-1600 °C interval. β Si_3N_4 , or the substituted β' Sialon derivative, grow with pronounced morphological anisotropy as hexagonal prismatic crystals elongated in the c direction. The faceted anisotropic form is inhibited by neighbouring grain impingement and hence is a function of residual liquid volume. The anisotropic morphology is the basis for enhanced fracture toughness but, for high temperature application, it is essential that the liquid, which normally cools to the glassy-state, is fully crystallised to form a diphasic ceramic (e.g. β' -YAG [Lewis et al 1980], Fig. 3).

A logical step in extending the quest for morphological anisotropy coupled with ease of fabrication is to utilise the glass-ceramic route (Fig.3). Silicate glass-ceramics are not sufficiently refractory, but oxynitride glasses may be crystallised to diphasic oxide/oxynitride microstructures with one of the phases in anisotropic morphology [Leng-Ward and Lewis 1985] - Fig.4. These glass-forming systems are based on eutectics which necessarily limits their stability at temperatures near to the liquidus ($\sim 1300^\circ\text{C}$).

Fig. 4

Electron micrographs of a range of ceramics taken from research programmes at Warwick University. a,b,c,d are monolithics with varying phase anisotropy and e,f are composites containing SiC in whisker and fibre morphology, respectively.



The microstructural parameters for 'monolithic' ceramics described above are determined by natural processes of crystal growth during sintering. These rarely have the optimised characteristics of critical phase dimension, thermal expansion differential, large morphological anisotropy, low interfacial cohesion and complete crystallinity. The artificial introduction of anisotropic phases into various matrices is an alternative fabrication process which has so far received limited attention. Ceramics with single crystal whiskers or amorphous fibres in glass-ceramic, nitride or carbide matrices are the most frequently studied 'composite' systems (Fig. 3 & 4). They offer the advantages of extreme phase anisotropy combined with low interface cohesion. However the ideal, non-reactive, interface may only be achieved via. low-temperature chemical-vapour infiltration (CVI) or via. the glass-ceramic process. There are obvious problems with reactivity in conventional sintering of high-temperature nitride or carbide matrices.

4. HIGH TEMPERATURE PROPERTIES

4.1. Fast fracture.

A comparative survey of fast-fracture parameters (MOR & K_C) for monolithic and composite ceramics is presented for a range of temperature (Fig. 5a, b). The two-fold increase in K_C for Syalon (Si_3N_4 - based) ceramics, sintered with a large liquid volume, over the hot pressed monophase ceramic is due largely to morphological anisotropy. A similar low K_C occurs for sintered silicon carbide which has a related microstructure (cf. Fig. 4a, b, c). The high temperature rise in K_C in ceramics which contain intergranular glass residues is due to enhanced grain pull out, crack-bridging and crack-blunting by viscous deformation above the glass softening point. This increment has little value due to severe creep-rupture problems in this temperature range.

Whisker or particle dispersions provide useful increments in K_C , typically 2-4x the monolithic matrix value. Examples are given for SiC whiskers in Al_2O_3 and Si_3N_4 ; the latter is reported with increments from zero to 10x and exemplifies the importance of processing conditions and interface cohesion. The potential of particle dispersions is demonstrated for TiB_2 in SiC; no attempt has been made to optimise particle size and anisotropy but the K_C value is comparable with cross-piled composites of continuous SiC fibres in glass-ceramic (LAS) or CVI-SiC matrices. A unidirectional SiC fibre/LAS glass ceramic composite is included in Fig. 5 but the K_C has no comparative meaning since it rarely fails by propagation of a single fast crack.

MOR values are frequently dominated by K_C (via. the relation, $MOR \propto \sqrt[1]{Y \cdot K_C \cdot C^{-1/2}}$ where Y is a geometrical parameter and C the critical flaw size) for ceramics of near-theoretical density and good homogeneity in which surface machining flaws are dominant. The poor values for cross-plyed Nicalon/CVI SiC probably arise from high porosity levels due to incomplete vapour-infiltration. The negligible influence of SiC whiskers in Si_3N_4 matrices is due to a compromise between K_C (in this case a 2-3 x increment) and the influence of whisker aggregates as large critical flaws. Hence one can explain the increase in Weibull modulus (m -Fig.5b) in specimens with a whisker filtration/screening step during processing.

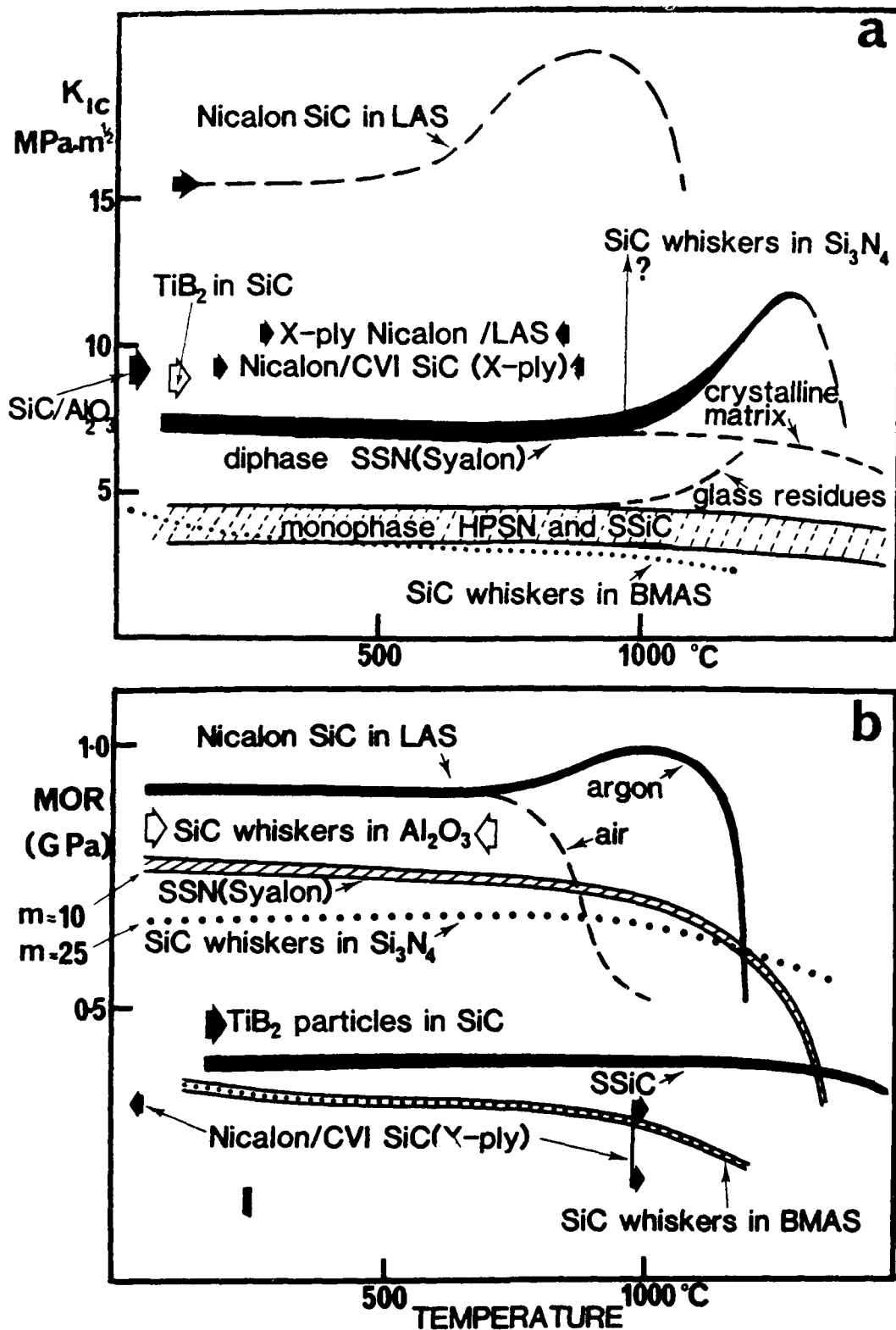


Fig.5.a.b.

A comparison of fast fracture parameters (MOR & K_{Ic}) for selected monolithic and composite ceramics, sampled from the literature: Nicalon in LAS (Brennan and Prewé 1982), Nicalon/CVI SiC (Caputo et al 1987), SiC in BMAS (Gadkaree and Chyung 1986), SiC in Al₂O₃ (Wei and Becher 1985), SiC in Si₃N₄ (Hayami et al 1986), TiB₂ in SiC (Janney 1987).

Creep-rupture comparison for a crystalline diphasic ceramic (β' -YAG) and a Si_3N_4 ceramic with glassy grain junction residues.



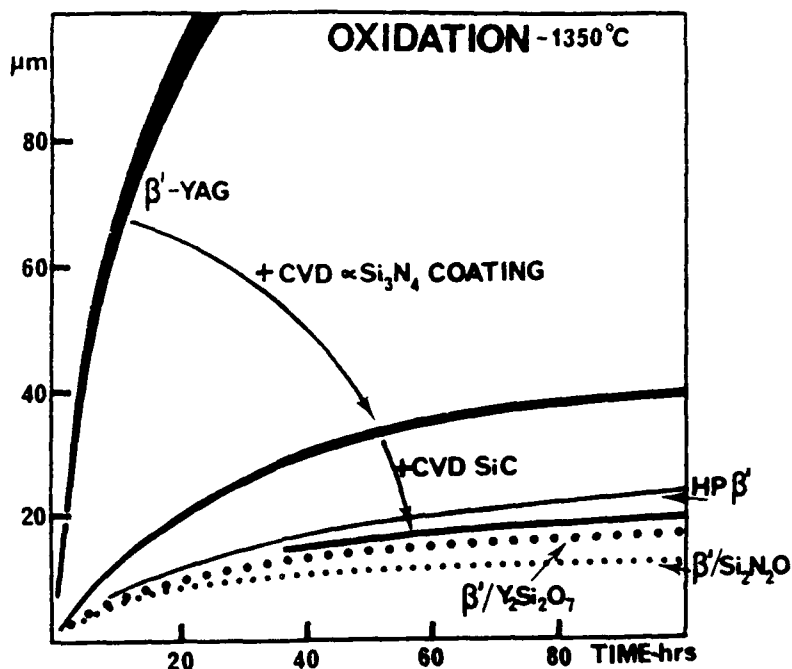
The success of composites in the high-temperature regime relies on the ability to use refractory matrices which are not susceptible to creep cavitation and the retention of non-reactive interfaces from the fabrication stage to long term application. Hence glass-ceramic matrices are unlikely to be useable above $\sim 1000^{\circ}\text{C}$ and for the more easily fabricated

non-stoichiometric compositions there is evidence for viscous flow of glass residues at much lower temperatures (e.g. the transient rise in K_C for Nicalon - LAS (Fig. 5) [Brennan & Prewé 1982]. Additional high-temperature instabilities exist in these materials due to, (i) crystallisation and loss of strength of Nicalon fibres above 1200°C and (ii) degradation of fibre-matrix interfaces in oxidising conditions (Fig. 5b) [Brennan & Prewé 1986]. SiC whiskers are normally stoichiometric pure carbide crystals which have good high-temperature stability compared to Nicalon (which is a non-crystalline oxycarbide). However, in whisker-composites the matrix-property is critical, since it is the major load-bearing component of microstructure. Hence glass-ceramic matrices are unsuitable for high-temperature engineering application (e.g. SiC in a Ba-stuffed cordierite - Fig. 5). The more promising alternative is that of whiskers or anisotropic particles within fully crystallised Si_3N_4 or SiC matrices, fabricated under high pressure sintering conditions at modest temperatures to inhibit interface-reactivity.

There are a number of remanent time-dependant problems within high temperature nitride ceramics initiated by environmental reactions. Firstly, in oxidising conditions certain phase combinations are intrinsically unstable. For example, oxide phases such as YAG react with the, initially protective, SiO_2 surface layer to form a eutectic liquid above 1300°C. [Lewis et al 1981] Oxidation rates increase catastrophically (Fig. 7) and the formation of liquid intrusions is detrimental to creep-rupture (Fig. 6). A partial solution is provided by CVD coating with Si_3N_4 or SiC, the reduced oxidation rate being comparable with hot-pressed monophase ceramics or those with second phases in which metallic ions are retained in a stable state (e.g. $\text{M}_2\text{Si}_2\text{O}_7$).

Fig. 7.

Comparison of oxidation kinetics for Si_3N_4 - ceramics with different phase combinations in surface microstructure



A related environmental - degradation problem occurs in corrosive conditions, exemplified by the large decrement in strength of nitride ceramics exposed to NaCl - containing atmospheres in a simulated gas-turbine combustor [Reed 1987]. This results from accelerated oxidation due to reduced viscosity of the SiO_2 protective layer when it contains Na & Cl ions. The oxidation rate is amplified at microstructural heterogeneities, such as a localised excess of second phase, generating hemispherical pits which act as stress-concentrating Griffith flaws.

5. CONCLUSION

The identity of mechanisms for toughening and for high-temperature creep and creep-rupture of ceramics results in guide-lines for model microstructures. They are preferably diphasic with one of the phases having an extreme morphological anisotropy, both phases being totally crystalline and stable in a variety of service environments. A compromise in terms of ease of fabrication, fracture toughness and high-temperature stability is obtained via. the liquid-phase-sintered 'sialon' compositions in which the residual liquid is crystallised during post-sintering heat treatment. Some improvement above the $\sim 1300^{\circ}\text{C}$ stability limit for nitride ceramics is obtained via. H.I.P.- sintering with crystallisable M-Si-O-N liquids of low volume, but a reduced toughness results from loss of anisotropy in the major phase (Si_3N_4). A similar problem occurs with solid-state-sintered SiC ceramics which currently are the only contenders for engineering application above 1400°C in oxidising environments.

Artificially induced diphasic ceramics, with anisotropic particles, whiskers or semicontinuous fibres in a refractory matrix offer the greatest potential for significant increases in toughness. However, fabrication of these refractory composites with the necessary non-reactive interfaces and their instability, particularly in oxidising conditions, are examples of the many problems which are currently without solution.

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CERAMIC-CERAMIC COMPOSITES FOR USE AT HIGH TEMPERATURE

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INTRODUCTION

Ceramic fiber reinforced ceramic is an emergent class of materials in which great hopes are placed, mainly to solve the need for new materials in the realization of great projects such as, for example, Hermes or ramjet engines. In addition, they are being considered for solving various problems related to high temperature applications in which thermostructural (turbojet and motor engines) or special (electromagnetic wave absorption) properties need to be introduced.

These uses mainly require low weight, high strength, high toughness, high temperature resistance, thermocycling resistance, damage resistance, sometimes high emissivity, often large structures and always reproducibility.

In a first approach, the realization of such materials seems to be a difficult challenge. My purpose is to analyse the present state of the art and try to specify the limits of such a challenge and the trends for the future.

This analysis deals with the high temperature range between 1000 and 2000°C, for which chemically aggressive environments can be extremely detrimental to materials. In order to treat this subject more realistically, the conditions of use will be based on the above examples such as thermal protection systems for hypersonic glider and ramjet combustion chambers, in which large structures are needed.

1. MECHANICAL RESISTANCE AND RELIABILITY OF COMPOSITES

Before developing the high temperature aspect, it is important to recall the kinds of problems which are solved or introduced with the composite approach.

The analysis of the evolution of ceramic structural properties during the last four decades (Fig. 1) shows that their strength was continuously in progress until 1979. On the other hand, their toughness has remained at the same level since 1960. This trend is explained by continuous progress in the flaw control of intrinsically low K_{Ic} materials. So, for a long time the

brittleness prevented the use of ceramics in systems where reliability was a prime necessity.

By 1980, significant progress had been made in terms of toughness with the advent of ceramic composites. Rapid evolution resulted from a better understanding of the toughening mechanisms such as:

- phase transformation and micro-cracks at the crack tip;
- crack branching;
- load transfer in fibrous composites;

but also from the development of several technologies connected with the field of composites:

- high performance fibers (carbon, SiC, alumina...);
- chemical vapor and liquid precursor infiltration (carbon, SiC, oxides...);
- multidirectional waving.

What is the import of such an increase in toughness for brittle components composites?

First, the linear approach gives a clear distinction between brittle and non-brittle matrix composites. The comparison of stress-strain diagrams (Fig. 2) shows that this distinction is based on the difference between fiber and matrix ultimate strains. It also shows that the increases of fiber modulus (E_f) and concentration (V_f) correspond to a proportional increase in the stress on the composite (σ_{cu}) at which the matrix cracks (σ_{mu}). This supposes an ultimate strain of the fibers which is higher than that of the matrix, and also interfacial conditions which allow sliding when a matrix crack reaches the fibers.

Nevertheless, this approach is inadequate to explain several phenomena revealed by the actual stress-strain diagrams (Fig. 3):

- increase in the matrix ultimate strain (ϵ_{mu}) when the fiber concentration (V_f) increases;
- non-linear evolution during multicracking;
- hysteresis loops after multicracking.

A theory was first developed by Aveston, Cooper & Kelly to explain the multicracking mechanism [2], which relates the distance between cracks (X) to specific composite characteristics:

* From R. RICE : Ceramic composites, a major material opportunity (NRL 1983)

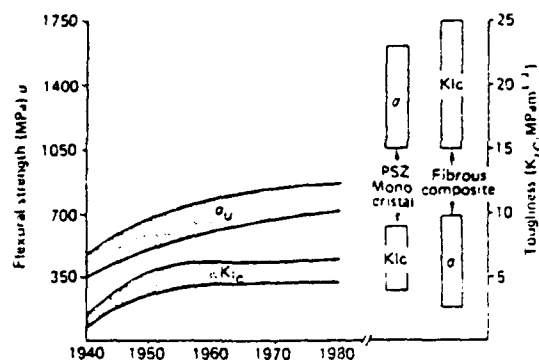


Fig. 1. Evolution of the strength and the toughness of ceramics during the last four decades*

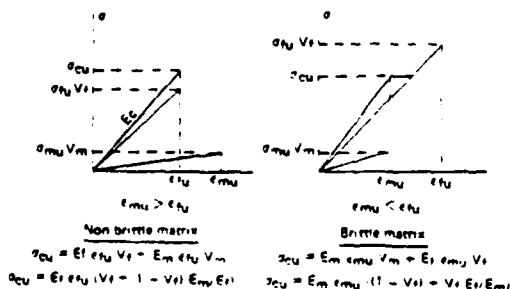


Fig. 2. Linear stress-strain diagrams of unidirectional composites under tensile stress

$$X = \frac{\phi_f \sigma_{mu} (1 - V_f)}{4 \tau V_f}$$

where ϕ_f Fiber diameter
 σ_{mu} Ultimate strength of the matrix
 τ Ultimate sliding strength at the interface

More recently, a statistical approach of the rupture of such composites [3] has given a satisfactory explanation for the above-mentioned phenomena. Fig. 4 and 5 present such statistical stress-strain diagrams of SiC/LAS and SiC/SiC composites. They show the sensitiveness of the fiber content to the critical strain (when the first crack appears) and of the ultimate sliding strength at the interface to non-linear behaviour after the first crack respectively.

This approach introduces the dimension effects at microstructural level inside the composite and flaw effects either inside the matrix or in the fibers. It is also clear that the high toughness of ceramic composites requires simultaneously:

- an ultimate strain of the reinforcement higher than that of the matrix;
- interfacial conditions which allow sliding when cracks reach the fibers;
- matrix multicracking and fiber bridging;
- consequently, a progressive vulnerability function of the stress beyond the critical strain.

Nevertheless, this last remark must be clarified because it is directly related to the propagation mode of cracks in the matrix. The statistical

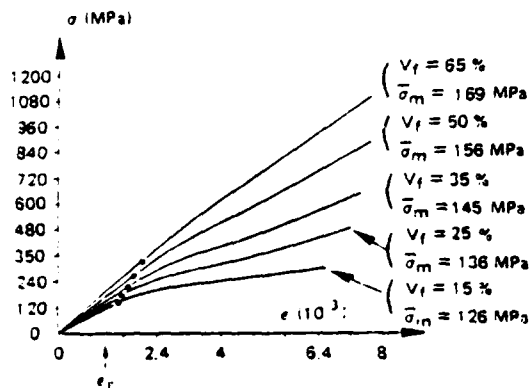


Fig. 4. Statistical stress-strain diagrams of unidirectional SiC/LAS composite: fiber content sensitivity

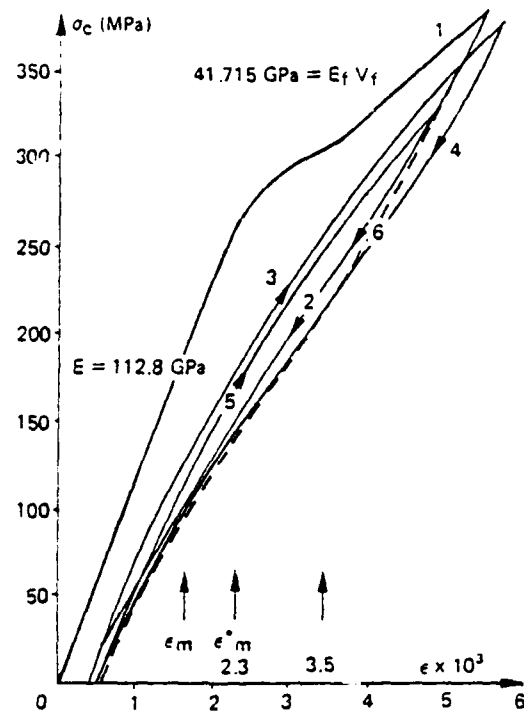


Fig. 3. Experimental stress-strain diagrams of an unidirectional SiC/LAS composite [1]

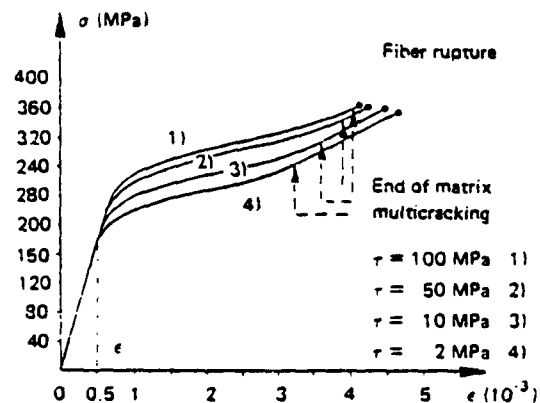


Fig. 5. Statistical stress-strain diagrams of SiC/SiC composite: sensitivity of the sliding strength at the interface

model is essentially representative of "crack initiation" in the matrix, and not of "crack propagation". Consequently, it fits the behaviour of composites for which the ratio $E_f V_f / E_m V_m$ is below unity very well, because in this case, the potential energy in the matrix before crack initiation is always higher than in the fibers. In such a case, the energy available in the matrix is generally sufficient to develop full propagation in the matrix. Such a behaviour has been identified for instance in SiC/SiC and in some carbone/SiC composites. The behaviour is not necessarily the same if the ratio is above unity because, for a given stress, the energy available in the matrix after initiation may be insufficient to cause the propagation. In particular, this is true when the matrix shows a pronounced subcritical behaviour. SiC/LAS composites are a good example, in which it is possible to delay large cracks when V_f is sufficiently large. In other words, vulnerability of ceramic composites is not an inevitable result of multicracking.

2. BASIC CONDITIONS OF COMPOSITE SURVIVAL IN THE 1000-2000°C RANGE

In the high temperature range, the basic condition for composite survival is mainly the chemical compatibility of components to insure the internal stability of the material. The first concern reentry vehicles and rocket nozzles, which required very high temperature materials (2000 to 4000°K) for a limited time (a few minutes). They have to withstand erosion and oxidative ablation, and to support relatively high mechanical stresses. The best material developed to do that was the carbon/carbon composite, which is chemically homogeneous.

Whereas this material exhibits excellent mechanical characteristics up to 2000°C in reduced atmosphere (fig. 6), it is very sensitive to oxygen and it cannot be considered a permanent material, unless efficient protection can be developed for this kind of composite. This is the first possible approach which is interesting to analyze.

The second example concerns ceramic composites using refractory components such as oxides, carbides or nitrides. For this class of materials, which are being extensively investigated, the first identified high temperature limitations are related to:

- the intrinsic stability of the components (grain growth, creep...);
- diffusion or reactions between components (interface control);
- fiber sensitiveness to external species (oxidation resistance);
- diffusion of these external species through the matrix;
- reactions between matrix and external species.

All these parameters can define the intrinsic temperature/time stability domain of a given system which will be reviewed later.

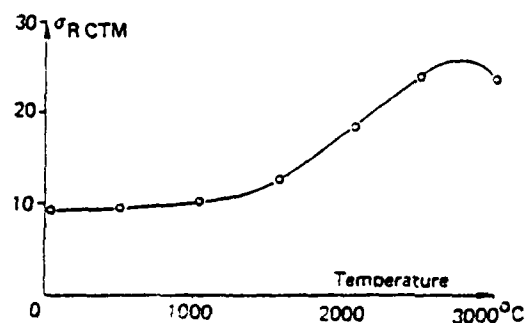


Fig. 6. Evolution of the shear strength of 3D carbon-carbon composite with temperature

Now, inside this previous domain and under mechanical loading, how is it possible to maintain strength and toughness? When the critical stress is reached in the matrix, microcracks begin to expose simultaneously interface and fibers, and can consequently thoroughly modify the composite rupture

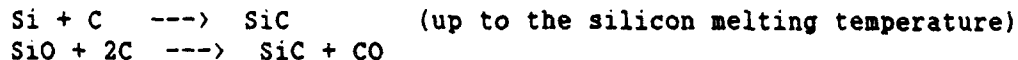
behaviour if their sensitiveness to external species is high. Unfortunately, this is the most frequent case, and the solutions concern either the fibers (coating technology to extend the capabilities of available and future ceramic fibers) or the whole surface of the composite (external coating sufficiently soft to insure the cicatrization of microcracks, like in carbon-carbon protection).

3. PROTECTED CARBON-CARBON COMPOSITES

Presently, there are several ways to protect carbon against oxidation. They depend upon the nature of the carbon (glassy carbon, polycrystalline graphite, pyrolytic carbon...) and mainly upon the temperature range of use. For the 1000-2000°C temperature range and prolonged use, the most common method is based on silicon compound coatings chemically compatible with the carbon because of possible formation of an SiO_2 protective layer by oxidation. This better compatibility of silicon compounds with the carbon is obviously guaranted with the covalent silicon carbide. Nevertheless, it has intrinsic limitations that will be analysed later. In addition, to achieve satisfactory efficiency of such a method under severe thermochemical environments, many technical difficulties have to be solved simultaneously, such as:

- chemical bonding between carbon and silicon carbide coating;
- thermomechanical adequation between the composite surface and the coating;
- gas-tightness all over the exposed surfaces;
- in-depth protection to avoid rapid oxidative collapse.

Presently, the relatively good results have been obtained with various SiC processing techniques on the composite surface. The diffusion concerns a depth of several hundred microns, which realizes a porous SiC bed. Two main siliconizing methods are available. They are based upon the following reactions with carbon:



Nevertheless, to meet the above conditions, the SiC bed has to present several characteristics:

- homogeneization and reduction of Young's modulus at the surface level;
- progressivity of the transition between carbon and SiC ;
- a first protection able to avoid rapid oxidative collapse;
- conditions to receive an overcoating able to guarantee the gas tightness.

Generally, such a bed cannot maintain full protection during a long period, but is able to considerably reduce the oxidation rate of the composite and may be considered as an in-depth protection. To obtain full protection during a long time inside the limits of thermodynamic stability of such a system, the previous bed has to receive an overcoating. This is a more critical phase, because the choice of this overcoating is connected with several parameters depending on:

- the mean elastic properties of the carbon-carbon (mean Young modulus),
- the stress mode (tensile, compressive, shear),
- the thermal and mechanical stresses,
- temperature and thermal shock, etc....

In other words, two main approaches can be used to choose the technology of this overcoating:

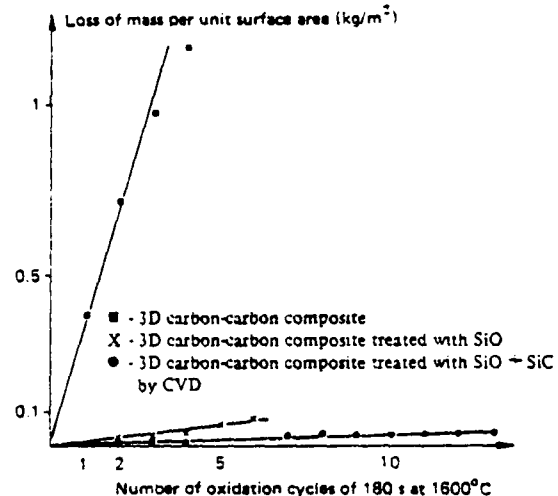
- SiC CVD coating under low pressure to develop a good infiltration is the best solution, for high temperature and low pressure and mechanical stresses;
- silica or silica glasses introduced by sol-gel route is a good solution in the opposite case.

The following mass loss rate diagrams (Fig. 7) compare the behaviour of a 3D carbon-carbon composite [4]:

- without treatment,
- with SiO treatment,
- with SiO + SiC CVD treatment.

Fig. 7. Comparison between mass loss rates obtained by thermal cycling at 1600°C in air at atmospheric pressure on 3D carbon-carbon respectively:

- without protection
- after SiO treatment
- after SiO and SiC CVD treatment



They were obtained by thermal cycling (500°C/min) between 100 and 1600°C (held for 3 min), in air at atmospheric pressure.

The following micrographs (Fig. 8) give some details of the above protection.

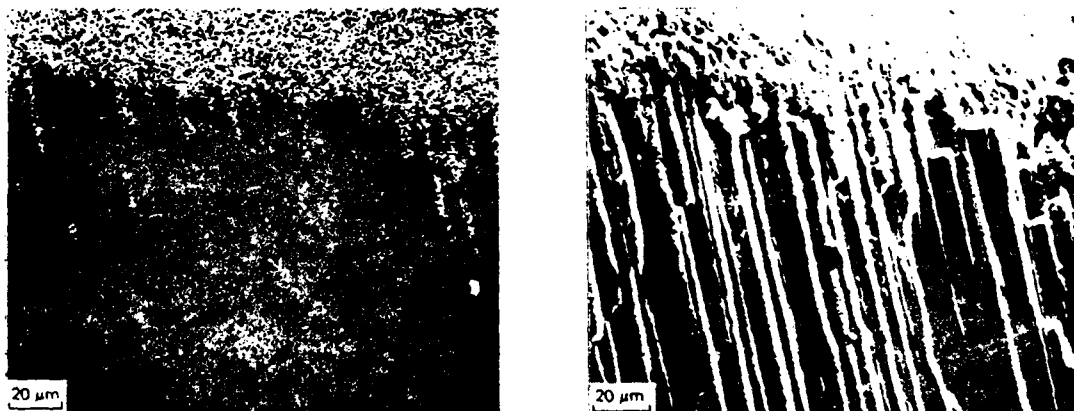


Fig. 8. Micrographs of a 3D carbon-carbon protection obtained after SiO and SiC CVD treatments and oxidation

This is an encouraging result, but still imperfect. Nevertheless, it was obtained on the most critical architecture that a carbon-carbon can present (Fig. 9).

4. THERMOMECHANICAL POTENTIALITIES OF CERAMIC COMPOSITES

The previous analysis of section 2 emphasized the basic conditions of composite survival in the high temperature range. They are presently reviewed through the thermomechanical properties of available ceramic fibers and some ceramic-ceramic composites.

4.1. Thermomechanical properties of ceramic fibers

Of the current commercial ceramic and carbon fibers presented on the following strength-Young's modulus diagram (fig. 10), few are suitable to receive a ceramic matrix because the processes impose temperatures up to 1000°C. Presently, most of the ceramic-ceramic research and development mainly concerned:

- high strength or high modulus carbon fibers ($d = 1.7$ to 1.9);
- silicon carbide fibers (Nicalon, Tyranno or CVD-AVCO) ($d = 2.5$ to 3.2);
- accessorially, mullite or alumina fibers (3M, Sumitomo, Du Pont) ($d = 3.1$ to 4).



Fig. 9. Macrograph of a 3D carbon-carbon composite surface

Their strengths are between 2000 and 3300 MPa, their modulus between 200 and 450 GPa.

Whiskers, in terms of thermal stability (monocrystals), their strength and modulus are theoretically remarkable. For example, Los Alamos SiC whiskers exceed a strength of 21 GPa and a modulus of 700 GPa. When their fabrication will be commercially developed to achieve sufficient lengths, adequate packaging, low cost and availability, they will compete favorably the best previous long fibers in ceramic-ceramic processes. Presently, very encouraging results have been obtained for composites with various matrices [5,6,7] and SiC whiskers.

For example, alumina-reinforced SiC whiskers (15% volume) reach a flexural strength of 650 MPa with a fracture toughness of 4.6 MPa \sqrt{m} , and the creep rate at 1500°C is reduced by several orders of magnitude (creep stress exponent of 5, activation energy of 450 kJ/mole and strains to failure of 3-4%). Such processes using hot pressing or hipping are suitable for making small pieces, which are interesting for engine applications (turbine blades). Nevertheless, in terms of large structures this class of composites is still considered brittle and not reliable enough.

However, the variations with temperature of the ultimate strength of previous continuous fibers are very different (fig. 11): whereas carbon fibers are quasi-insensitive to temperature in reducing atmosphere, ceramic fibers begin to lose their strength from 900°C, but maintain their modulus up to this temperature. From this point of view, SiC CVD fibers are presently the best in spite of their microstructural change, but they have two main disadvantages: their difficult use and their large diameter (140 μm). Now, SiC Nicalon fibers present important advantages (low diameter, weavability) and are presently the most investigated for ceramic composites. Nevertheless, their strength sensitiveness to oxidation is widely reported

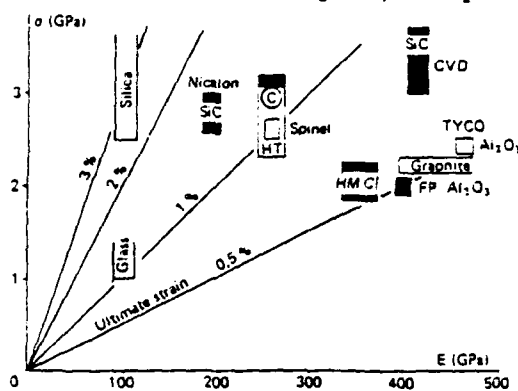


Fig. 10. Mechanical properties of current commercial ceramic fibers

[8,9,10] and begins at 600°C. In terms of high temperature stability, recent investigations have shown that they are largely perfectible [11]. So, in a reducing atmosphere, their strength can be maintained (90-93%) up to 1350°C, after long heat treatments (several hours). Nevertheless, during such treatments, they produce some SiO₂, a very thin carbon coating (100 Å) and a light SiC grain growth. Now, new similar fibers produced from an organometallic precursor are presently in development (Ube, Avco, Rhône Poulenc, Dow Corning MPDA, HPZ and MPS). Their improvement is essentially based on titanium (Ube) or nitrogen (R.P. and D.C.) additions to reduce grain growth at high temperature. Simultaneously, a large effort is performed to reduce the oxygen content (as silica), which is liable to react at high temperature either with free carbon or amorphous SiC [12]. It is too early to know their high temperature performance and their impact towards effective ceramic matrix reinforcement.

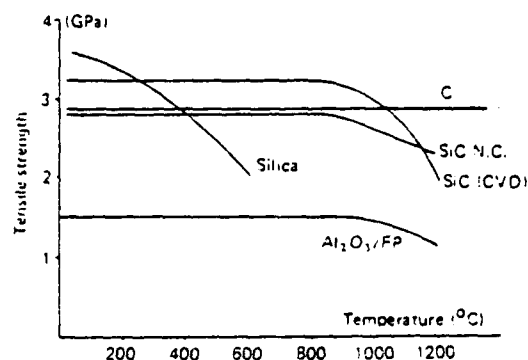


Fig. 11. Thermomechanical properties of some ceramic fibers

Oxide fibers are very sensitive to grain growth and creep when a glassy phase is present. They have been largely used in recent research programs, but have always presented disappointing behaviour, and especially in oxide matrix composites, because of fiber-matrix interactions of particular importance [13]. Like SiC fiber manufacturers, 3M and Du Pont are presently developing new oxide fibers (Nextel 480 and PRD 166). The first is mullite (+ 2% B₂O₃), the second is α -alumina with Y₂O₃ partially stabilized ZrO₂ as a second phase [13]. All these modifications were made to improve their strength retention after exposure to high temperature through a presumable grain growth inhibition. Here too, it is too early to know their high temperature behaviour in ceramic composites. Nevertheless, recognizing the need for more refractory ceramic fibers, all these suppliers are working toward improved products.

4.2. High temperature properties of ceramic composites above 1000°C

For continuous fiber reinforcement, several fabrication techniques have been used for carbide, silicate, oxycarbonitride and nitride matrices. Descriptions of specific combinations of fibers, matrices and processing conditions have been recently reviewed [14,15,16]. Data on the high temperature mechanical properties of the corresponding composites are limited. However, with SiC/glass ceramic composites several authors mention a rapid degradation occurring above 1000°C in air [17] and transition in tensile failure mechanism to a brittle mode of failure occurring above 800°C in air [18]. So, among all these combinations, SiC/SiC and C/SiC [23] seem to be the only composites able to sustain use beyond 1000°C.

The Nicalon 2D reinforced SiC CVI composite (Cerasep 320, 7-86 data) has a density of 2.50 and a critical stress of 100-110 MPa (beginning of multi-cracking). Its ultimate tensile strength is 210-230 MPa. The intrinsic oxidation resistance of such a composite is given by residual strengths after oxidation treatments in air (table 1).

Temperature treatment (°C)	Time of treatment (h)	Residual strength (MPa)
1100	100	200
1200	100	170
1200	400	160
1450	50	110

Table 1. Residual strengths of Cerasep 320 after oxidation (*)

Pre-loading (MPa)	Oxidation temperature (°C)	Oxidation time (h)	Residual strength (MPa)
70	1200	0.5	230
105	1200	0.5	221
130	1200	0.5	111
105	1100	100	148

Table 2. Residual strengths of Cerasep 320 after preloading and oxidation (*)

After these oxidations, the toughening mechanism is maintained, but degrading of fibers would be responsible for a decrease in strength. The second investigation concerns oxidation vulnerability after preloading below and above the critical stress.

Here too, the toughening mechanism is maintained, but the oxidation effect is drastic above 105 MPa. To improve this composite, SEP has developed a very efficient oxidation protection which does not modify the toughening mechanism up to 1400°C (fig. 12).

In such conditions, Nicalon fibers are able to maintain ultimate strain up to 0.7%. This verifies the previously announced potentialities of this class of fibers up to 1400°C if they are used in an adequate environment.

The carbon 2D reinforced SiC CVI composite (Sepcarbinox 111, 7-86 data) is a very thermostable system. High temperature strengths measured in an inert atmosphere are quasi-independent of the to 2000°C (table 3).

Toughening is maintained up to 2000°C, but as in the previous one, it needs an oxidation protection. In other words, SiC/SiC may be used safely up to 1300°C with reliability up to 1550°C and C/SiC may be used safely up to 1600°C after protection with reliability up to 2000°C.

5. HIGH TEMPERATURE KINETICS OF OXIDATION AND NITRIDATION OF SILICON CARBIDE

Silicon carbide is extensively used both in the protection process of carbon-carbon and in ceramic-cera-

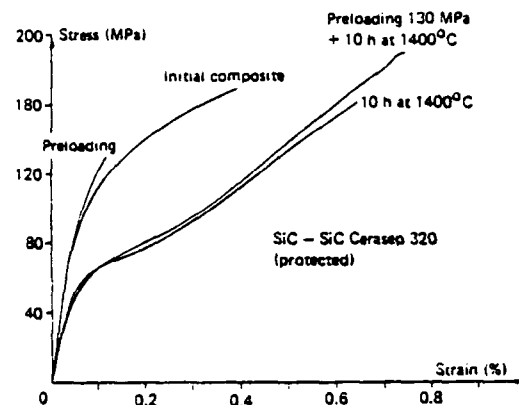


Fig. 12. Thermomechanical behaviour of protected Cerasep 320 after preloading (130 MPa) and oxidation for 16 hours at 1400°C

Sollicitation mode	Temperature (°C)	Strengths (MPa)
Tensile	20	350-400
"	1200	450-500
"	1600	310-320
Flexural	20	450-500
"	1300	650-700
"	2000	400-450
"	2200	250

Table 3. High temperature tensile and flexural strengths of Sepcarbinox 111 in an inert atmosphere (*)

(*) Data published with permission from SEP

mic composites (SiC/SiC, C/SiC); some aspects of the high temperature kinetics of oxidation and nitridation of SiC, in molecular and dissociated oxygen and nitrogen under low pressure are recalled below. This environment is the one of hypersonic gliders such as Hermes.

Many investigations were performed in the last twenty years on this subject in molecular air under atmospheric pressure, but few of them concern SiC behaviour in dissociated air under low pressure. The results of such an investigation [19,20] on SiC CVD have been summarized later and used to approximate the erosion rate of this material during the most critical phase of Hermes reentry.

Experimental conditions used for this investigation allowed chemical kinetic measurements free of the intervention of gas phase diffusion phenomena to be obtained between 1750 and 2400°K and between 10^{-3} and 1 torr.

The main results show that:

- the transition between passive and active oxidation reactions of the SiC cannot be thermodynamically defined, but is determined only by the existence or non-existence of the protective silica coating, which can evaporate under high temperature and low pressure conditions (vapor pressures of silica are typically: 10 torrs and 1732°C, 40 torrs at 1867°C and 100 torrs at 1969°C);
- dissociated oxygen favorably shifts the p-T locus at the active-passive transition;
- up to this p-T locus, removal rates are independent of temperature and pressure;
- dissociated nitrogen produces approximately the same effects as dissociated oxygen;
- in the passive domain, mass loss rates under N + O equimolar mixture flow can be more than one decade below the one under pure N or O flows. This is explained from the presence of silicon oxinitrides, which are known for their higher vaporization behaviour compared with silica.

From these experimental removal probabilities (ϵ), we formulated their analytical expressions after some simplifications of the network (Fig. 13).

The following expression does not integrate the favourable N + O coupling but, in first approximation, can be applied to N, O atoms and molecular oxygen:

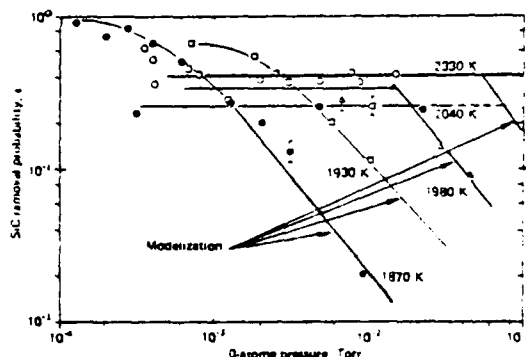


Fig. 13. Dependence of SiC CVD oxidation probabilities on O atom pressure and possible modelization

$$\epsilon = \frac{\phi_{\text{SiC}}}{\phi_1} = \frac{0.1}{10} \cdot 10^{-7.23 \log P} \cdot 10^{-\frac{-21.81 + 4.12 \cdot 10^4/T}{10}}$$

Mass flow rates of gaseous species near the surface at the nose stagnation point were determined from a boundary layer program based on the Gardiner model with catalytic or non catalytic wall. For 80 km altitude, 26mach, the wall pressure is 7.3 torr, and for a wall temperature of

Wall	N	O	$P_o / (P_o + P_N)$
Catalytic	2.11 E^{-3}	1.09 E^{-2}	0.81
Non catalytic	2.64 E^{-3}	1.77 E^{-2}	0.37

2100K only dissociated species (O and N atoms) impinge on the surface with the following mass flow rates per unit area (kg/m.s).

Under these conditions, the corresponding erosion rates are 83 and 1 micron per hour respectively. Since this corresponds to the most pessimistic assumptions of the past SiC (without protection) use, that could not co-exist in a real configuration, the reality would be somewhere between these two rates. Consequently, silicon carbide can be considered as a possible material for the reusable thermal protection system for a hypersonic glider like Hermes. Nevertheless, this has to be confirmed on real composites, for which porosity, rupture behaviours and total emissivity can have a significant impact on oxidation damage and on equilibrium temperature levels respectively.

For applications in which the pressure is high (above atmospheric) and the air is not dissociated (case of ramjet combustion chambers), SiC works in the "passive reaction" domain up to 2300K with very low erosion rates directly controlled by diffusion kinetics. This domain is relatively well known [21,22].

6. CONCLUSION

Presently, carbon and silicon compounds (especially silicon carbide and its silica protective layer) seem to be the two main materials able to maintain very high temperature stability and thermostructural properties of composites simultaneously beyond 1000°C in spite of their oxidation sensitivity. With additional protection, SiC/SiC CVI and C/SiC CVI can be used safely over their critical stresses respectively at 1300 and 1600°C. They can also sustain higher temperatures for a brief time.

C/C composites can be used beyond 1600°C with efficient protection. Silicon compound protective systems have made great strides and this special class of ceramic-ceramic composites remains a very promising one.

Nevertheless, beyond 1600°C in low pressure and dissociated environments, SiC composites have to be investigated in more detail.

SiC Nicalon for long fibers and SiC whiskers are the main ceramic reinforcements successfully used to date with various ceramic matrices. The first may be used up to 1350°C if its protection is insured. The second is very attractive for higher temperatures, and especially the hot spots of engines. Fiber suppliers have now recognized the need for more refractory products and are working toward improving them.

Below 1000°C, ceramic composites are in progress and reinforced glass-ceramic composites presently show the most advantages (performance/ price) in this range.

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Development of composite high temperature materials for future energy conversion applications.

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ABSTRACT: At high temperatures monolithic materials can no longer fulfill all requirements posed by advanced energy conversion applications. It will be shown how diffusion couples can be used to study metal-ceramic interactions and to develop composite materials. Attention is paid to the development of a hot shell for a combustion heated thermionic energy converter operating at 1450°C. It will be shown how the combination of chemical and physical requirements leads to the design of a trilayer material, consisting of a W emitter, coated with a diffusion barrier of TiN and an outer protective shell of SiC.

1. INTRODUCTION

In Eindhoven research and development of ceramic materials is performed in the Centre for Technical Ceramics, CTK. This is a joint venture of the Department of Physical Chemistry of the Eindhoven University of Technology and the Ceramics Department of the Institute of Applied Physics TNO. The work ranges from basic research aimed at applications for the future to short term projects for solving well defined industrial problems. Part of this article will be focussed on the materials problems which have to be solved during the development of a combustion heated thermionic energy converter (TEC). In such a device heat is converted directly (without moving parts) into electricity. Basically the TEC is a diode in which one electrode is heated sufficiently (about 1700 K) to thermally emit electrons (Figure 1). The other electrode, kept at a lower temperature, collects the electrons. Due to the different work functions of the two electrodes a potential difference is generated which can be subjected to an external load.

As the electrons need a finite time to reach the collector there is a certain density of electrons in front of the emitter. This cloud of electrons pushes the emitted electrons back to the emitter surface and limits the current density. This effect is called the space charge effect. To neutralize this effect cesium is introduced in the inter-electrode space. Cesium is a metal with a low melting point (27°C), reasonably high vapour pressure and, most important, it possesses the lowest ionization potential of all elements. Therefore, the Cs vapour will ionize partly at the hot emitter surface, forming a plasma, the positive charge of the cesium ions neutralizing the space charge effect. A TEC is a low voltage (0.5V), high current density

(10 Amps/cm²) direct current power source. The principles of thermionic conversion are treated extensively in the literature (Hatsopoulos 1973, 1979).

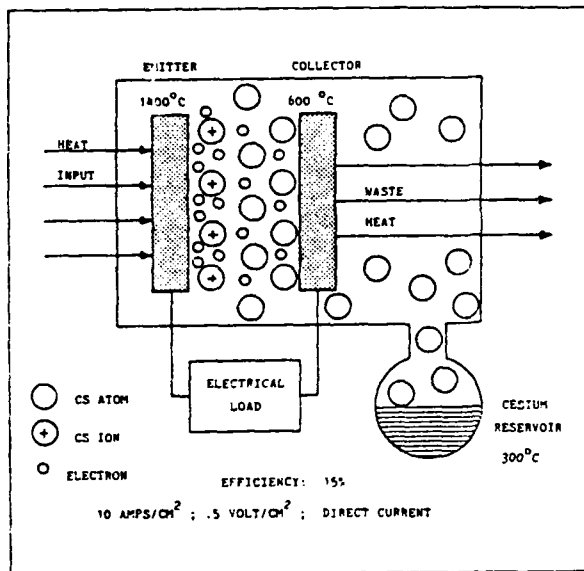


Fig. 1. Schematic drawing of a Thermionic Energy Converter.

It is our aim to build a combustion heated converter. The design is shown schematically in Figure 2.

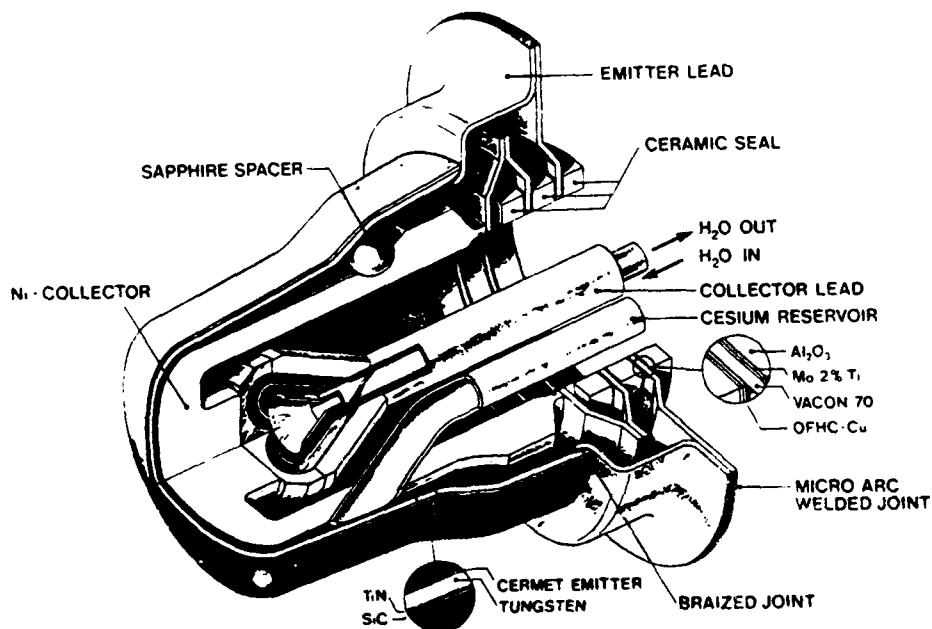


Fig. 2. E.U.T. Design of a combustion heated thermionic energy converter.

An important part of the TEC is the "hot shell". This component serves a number of purposes at the same time. These can be listed as follows:

- protect the electrodes from the corrosive combustion atmosphere at temperatures up to 1450°C.
- function as a good electron emitter at the inside.
- function as electrical conductor with the lowest possible resistance at high temperature.
- supply the necessary mechanical strength to the device.

This means that it should be vacuum tight, cesium resistant, thermal shock resistant, have a good thermal conductivity and thermal emissivity. Furthermore, the hot shell has to be connected to the water cooled nickel collector by means of a metal-ceramic joint. The ceramic is needed to electrically isolate the emitter from the collector electrode. The technological demands encountered during this project have induced a number of fundamental studies. Firstly, we are studying the electron emission properties of different materials in a cesium atmosphere at high temperature. High temperature Cesium corrosion of ceramics is another research topic. Furthermore we study diffusion reactions between solids. The first and second topic are beyond the scope of this article, but we shall present some results of the diffusion studies in section 2. Next attention will be paid to the hot shell and metal-ceramic seals.

2. STUDIES OF REACTION DIFFUSION

In many high temperature applications of materials diffusive interactions play a decisive role. We will mention a few examples to illustrate this statement. In the thermionic converter the number of demands on the hot shell is so large that no monolithic material can be used. Therefore a multilayer material was designed. There are numerous other cases where coatings are used. It is also more and more

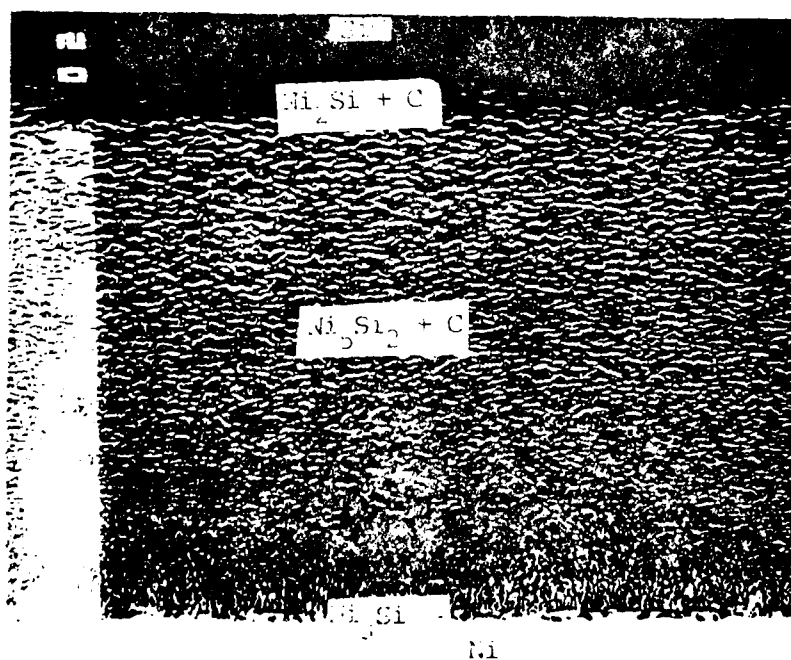


Fig. 3. Backscattered electron image of a diffusion couple α -SiC vs Ni, annealed 44.5 h at 850°C under a pressure of 13 MPa.
Bar = 100 μ m.

recognized that bulk ceramic materials are too brittle for many applications and thus composite materials have to be developed. Finally, ceramic materials often have to be joined to metals. Sometimes interactions have to be avoided, in other cases a certain interaction is desired. In this paper we discuss how diffusion couple studies can be used to obtain a better understanding of solid state interactions. As an example we first mention a study of the system α -SiC with different metals (Schiepers et al, 1987). To investigate the diffusion behaviour a disk shaped SiC platelet is pressed against a metal disk and heated in vacuum. After the heat treatment the diffusion couple is cut perpendicular to the interface and investigated using optical microscopy, X-ray diffraction and electron probe microanalysis (EPMA). Figure 3 shows an electron micrograph of a Ni-SiC couple.

As a starting material fully dense α -SiC was used, made by hot isostatic pressing without using sinter additives. Between SiC and Ni a reaction zone is observed, consisting of alternating layers of Ni_2Si (light coloured) and Ni_2Si with C precipitates (dark coloured), alternating layers of Ni_5Si_2 and $\text{Ni}_5\text{Si}_2 + \text{C}$, and finally a layer of Ni_3Si . The total thickness of the reaction layer after 44 h at 850°C is about $200\text{ }\mu\text{m}$. It is obvious that the rapid reaction prohibits applications of Ni in direct contact with SiC at this or higher temperatures. We have also performed these experiments with hot pressed SiC containing 0.45 wt% Al and with hot isostatically pressed SiC containing 0.2 wt% Al as sinter additive. In both cases the reaction rate is even higher than with pure SiC. More insight in the diffusion mechanism can be obtained by marker experiments. We have marked the interface between SiC and Ni by means of $5\text{ }\mu\text{m}$ diameter alumina particles. After the diffusion experiment the Al_2O_3 markers were found at the interface between the metal and the reaction layer as indicated schematically in Figure 4.

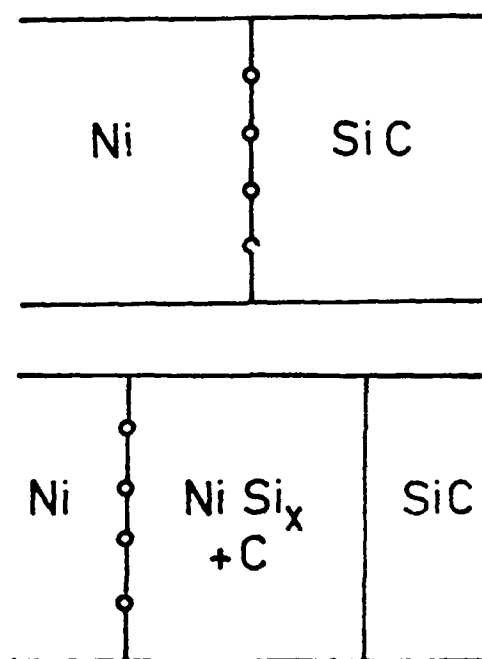


Fig. 4. Schematic representation of the morphology of a diffusion couple α -SiC vs Ni with Al_2O_3 markers. Top) before the diffusion experiment, bottom) after diffusion reaction.

From this experiment one can conclude immediately that only Ni diffuses and not Si and/or C! This implies that between SiC and Ni a diffusion barrier has to be used that hinders the diffusion of Ni and does not react with SiC. An example of such a barrier is TiC. The reaction between silicon carbide and nickel was described only as an example of the use of the diffusion couple technique. We have performed similar experiments with Fe, Ti, Mo and W at temperatures between 800°C and 1400°C.

Such studies give insight in the phase relations, the kinetics and in the morphology of the reaction layers. We have developed a theoretical model, base on thermodynamic data, to explain and predict the layer morphology (Van Loo et al 1984). It falls outside the scope of this article to discuss this point. However, it is evident that e.g. the mechanical properties of a reaction zone with parallel, straight interfaces are different from a zone consisting of two compounds with interwoven structure. For instance our example of Ni-SiC showed series of parallel reaction layers; the same was found for Fe-SiC or W-SiC. In the case of Mo-SiC, however, an aggregate structure is observed for one of the reaction layers (Figure 5). This is due to the fact that here carbon diffusion through the Mo_5Si_3 layer is the rate determining step (Van Loo et al., 1982).

A problem that pertains directly to the production of a thermionic energy converter is the development of the hot shell for this device. We will discuss this topic in the next section.

3. DEVELOPMENT OF A HOT SHELL

In section 1 we discussed already the requirements for the hot shell of a combustion heated TEC. One of the best electron emitters is tungsten. This metal can of course not be used in a combustion environment. As such SiC can be used. This material has an adequate cor-



Fig. 5 Electron micrograph of a Mo-SiC couple after 96 h at 1200°C.

rosion resistance, it has a high thermal conductivity even at high temperature (30 W/mK at 1400°C) and has a thermal expansion that matches quite well that of tungsten. From a diffusion couple experiment at 1200°C we found, however, a rapid reaction between SiC and W due to diffusion of Si. At this temperature a series of reaction layers is formed with the sequence W-W₂C-W₅Si₃-WC-SiC. Especially the formation of W₅Si₃ is detrimental since it has a low density, is very brittle and causes delamination. In the literature a hot shell is described consisting of a trilayer system tungsten, graphite, SiC. Although long lifetimes are cited (Goodale et al, 1984) this combination is thermodynamically unstable. In a diffusion couple C vs W we found a rapid diffusion of C, leading to the formation of W₂C and WC. For this reason we are now working with a trilayer system W-TiN-SiC. TiN is thermodynamically stable with respect to both W and SiC. Silicon diffusion through TiN can be neglected, carbon diffusion is slow and moreover the carbon activity of SiC is very low. Therefore TiN forms a good diffusion barrier. The most important problem is the difference in thermal expansion coefficient of the three components: SiC $4.5 \times 10^{-6} \text{K}^{-1}$, TiN $9.4 \times 10^{-6} \text{K}^{-1}$, W $4.45 \times 10^{-6} \text{K}^{-1}$. So far we have obtained good stability with 4 μm thick TiN layers. Figure 6 shows results of a diffusion experiment.

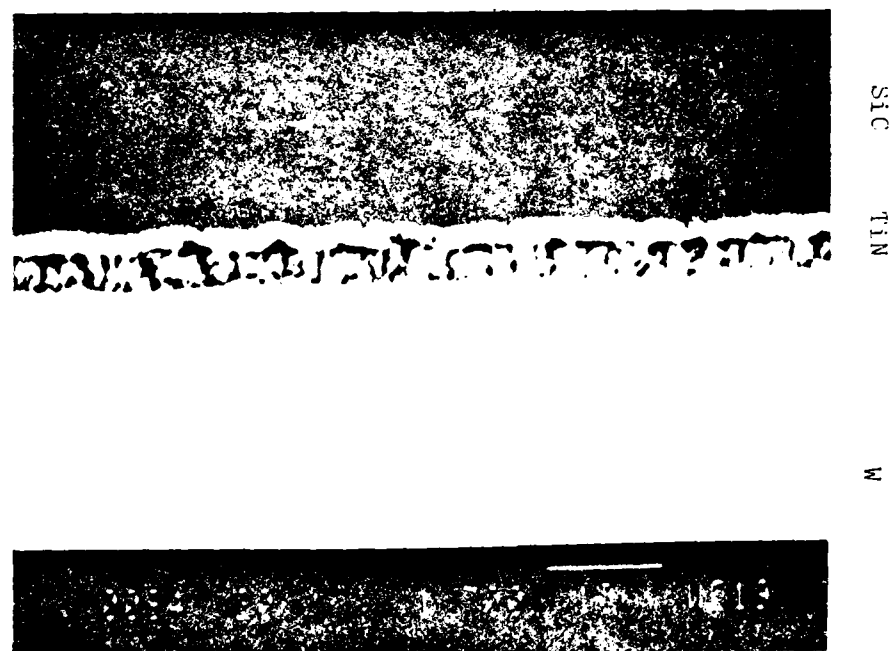


Fig. 6. Diffusion couple W-SiC with a 4 μm TiN diffusion barrier after 100 h at 1240°C. Bar = 10 μm .

No reaction can be observed after 137 h with a TiN diffusion barrier layer between W and SiC.

The experimental procedure for the production of the hot shell will be described only briefly. More details are given elsewhere (L.R. Wolff et al, 1987). Two routes are presently under development. For route 1 a plasma sprayed W shell is coated via chemical vapour deposition, first with TiN and next with SiC. The following experimental procedure is used. A brass mandrel is heated to 200°C and sprayed with a NaCl solution. On top of the 0.1 mm thick NaCl layer a 0.5 mm W layer is

deposited by plasma spraying. After cooling the mandrel can be removed and the NaCl is dissolved. The W is first reduced at 1600°C in hydrogen and next sintered in vacuum at 2200°C to 95% of the theoretical density. The W shell is covered at the outside with a 4 μm TiN layer by CVD at 850°C in a mixture of H_2 , N_2 and TiCl_4 . Subsequently a 300 μm SiC layer is deposited at 1100°C from a mixture of H_2 and $(\text{CH}_3)_2\text{SiCl}_2$. This layer thickness should be sufficient for a hot shell lifetime of 5 years at 1450°C.

At the same time we try to produce hot shells along a second route. First a free standing SiC shell is produced by CVD. Next the TiN barrier layer is deposited at the inside, in the same way as described above. Finally the W layer is produced by CVD from $\text{H}_2 + \text{WF}_6$ at 850°C.

In both cases leak tight hot shells were obtained, which were thermally cycled to 1600°C without problems.

Figure 7 gives an example of the final hot shell. The shell is already equipped with a Vacon 12S bellows. To this end the SiC is metallized and Cu soldered to the bellows.

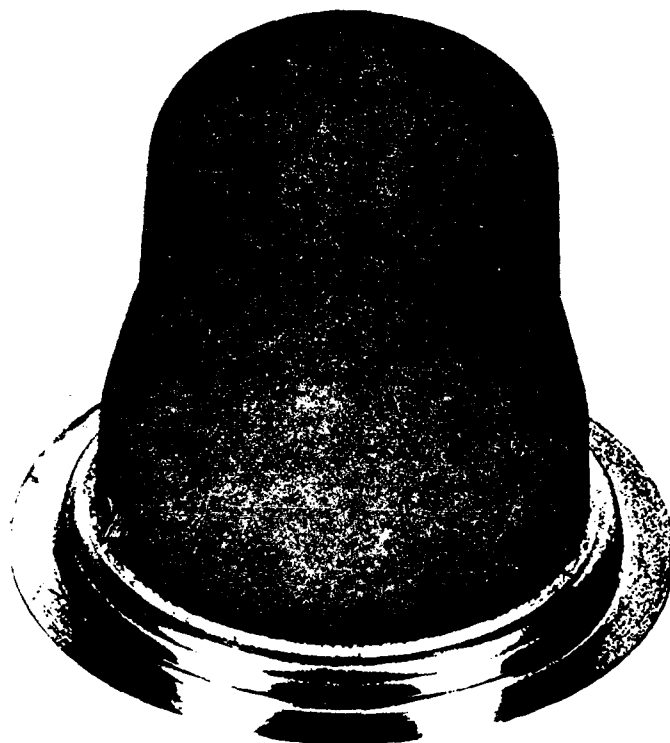


Fig. 7 Hot shell for the combustion heated thermionic energy converter.

We have described the materials aspects of the hot shell only. It will be evident from Figure 2 that many other problems have to be solved. Important is also the ceramic-metal joint which connects the hot shell to the collector by means of an electrically insulating seal. Since the operating temperature of this joint does not exceed 400°C we will not discuss it here. Another important point which has our atten-

tion is the emitter material. Although the first TEC's will have a W emitter, we believe that better results can be obtained with cermet emitters. We have already demonstrated that excellent emission properties can be obtained with W in an oxide ceramic. The presence of the oxidic phase ensures the formation of a W-O-Cs complex with an attractively low workfunction. Further improvement of the efficiency is expected if the emitter could be made of a directionally solidified metal-ceramic eutectic. In this way a needle like morphology is obtained, consisting of $\leq 1 \mu\text{m}$ diameter metal needles in a ceramic matrix. The fine needles cause an increased emission due to the field emission effect. We have developed a coating technique for producing such directionally solidified eutectics on refractory metal substrates.

4. SUMMARY

The combustion heated thermionic energy converter offers several interesting problems from the viewpoint of high temperature materials technology. Here, as in the majority of high temperature applications, corrosion and diffusion cause the main problems. We have tried to show that basic diffusion couple studies are an important tool in solving these problems.

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Limitations at High Temperatures of Present Day Engineering Materials

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1. INTRODUCTION

The major operational factors which determine material selection for high temperature operation are probably stress and environment. Although it is an oversimplification two basically different operational regimes can be considered. The first involves relatively high stress and a moderate temperature level which is consistent with the required life at the operating stress. Environmental influence is often a second order effect in such applications which include turbine discs in gas turbine engines. The second regime covers applications involving low stress and high temperature consistent with the environmental requirement. Applications such as heat treatment furnace hardware and gas turbine combustors fall into this regime.

The gas turbine engine has components whose operational requirements fall into both extremes and also components which operate in intermediate regimes, and will thus be used as the basis for discussing the limitations of current materials at high temperatures.

One of the major objectives in the design of advanced gas turbine engines, whether for industrial, marine or aero application is improved performance in respect of reduced fuel consumption and increase power/weight ratio. This results in several materials requirements with increased temperature capability being crucial.

The importance of high turbine operating temperature and the increase in efficiency which could be achieved if internal air cooling could be avoided in major turbine components are illustrated in Fig 1. Up to 20% of the compressor delivery air is used for component cooling in the latest engines.

The paper discusses the developments which have led to the current materials scene and highlights future requirements which cannot be met by current materials. The discussion centres around the three major engine components - turbine aerofoils, discs and combustors.

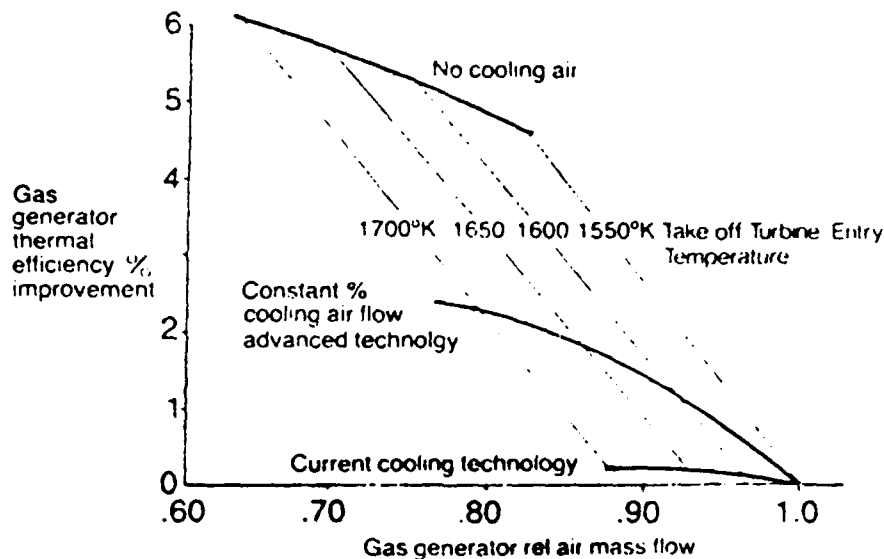


Fig. 1 Influence of turbine entry temperature and material/cooling technology on thermal efficiency.

2. TURBINE AEROFOILS

2.1 Materials

Nickel superalloys have been virtually the only materials used for gas turbine aerofoils and they have been developed in a process controlled sequence. Each new manufacturing process has allowed new alloy compositions to provide higher creep strength or has provided significant improvement in its own right eg the reduced Youngs Modulus in directionally solidified and single crystal materials.

The compositional changes necessary because of creep considerations have had relatively little effect on high temperature oxidation resistance but a marked detrimental effect on hot corrosion resistance. Such corrosion is experienced in the intermediate temperature range in salt contaminated environments such as in marine turbine operation and certain aero gas turbine operations. The use of less pure fuels in industrial gas turbines also results in a more aggressive corrosive environment. Such problems have motivated the development of cast alloys such as IN738 which have similar strength to some of the earlier cast alloys such as INCO 713 but significantly improved hot corrosion resistance.

Nevertheless corrosion resistant coatings are required to protect many blades in hot corrosion and high temperature oxidation environments. Aluminide coatings were first introduced in the early 1960's and are still in widespread use. Overlay coats of the MCrAlY type have been developed during the last decade and have been used in aero, marine and industrial engines. The thermal barrier coats which use a MCrAlY bond coat with an outer layer of zirconia and have been used on combustion chambers, will be used on turbine aerofoils in the future.

Following the use of conventionally cast and subsequently directionally solidified blades the most recent superalloy development to find application in turbine aerofoils are single crystals⁽²⁾

Several additional potential aerofoil materials have been proposed during the past decade. They include directionally solidified eutectics and mechanical alloys. These have not been used in production engine turbine blades although the mechanical alloy MA754 is used in stator aerofoils. The basic problems which have prevented the use of DS eutectics include solidification rates some one to two orders of magnitude slower than those used for DS superalloys and excessive property anisotropy. MA6000, the gamma prime containing mechanical alloy, appears to be limited to potential application in relatively lowly stressed aerofoil applications because of its limited strength at intermediate temperatures. In such aerofoils it could offer significant temperature advantage and its long term structural stability could well be a further advantage in industrial engines.

2.2 Blade Cooling

Since its introduction in the mid 1960's, aerofoil cooling technology has made a major contribution to increased turbine entry temperature on aero, marine and industrial aerofoils. A modern cooled cast blade is shown in Fig 2(a). There is a continuing need to improve cooling technology either to allow the use of higher turbine entry temperature or to reduce the cooling air needed for a given duty, thus increasing efficiency. Cooling efficiency in cast blades is limited essentially by the size and complexity of the cooling passages which are, in turn, limited by ceramic core and mould technology. Two advanced fabricated aerofoil concepts which allow the production of the cooling passages at an intermediate stage in aerofoil fabrication can provide increased cooling efficiency. These are wafer and spar/shell constructions (Fig 2b and 2c respectively). The cooling advantages of wafer blade technology were demonstrated some years ago.

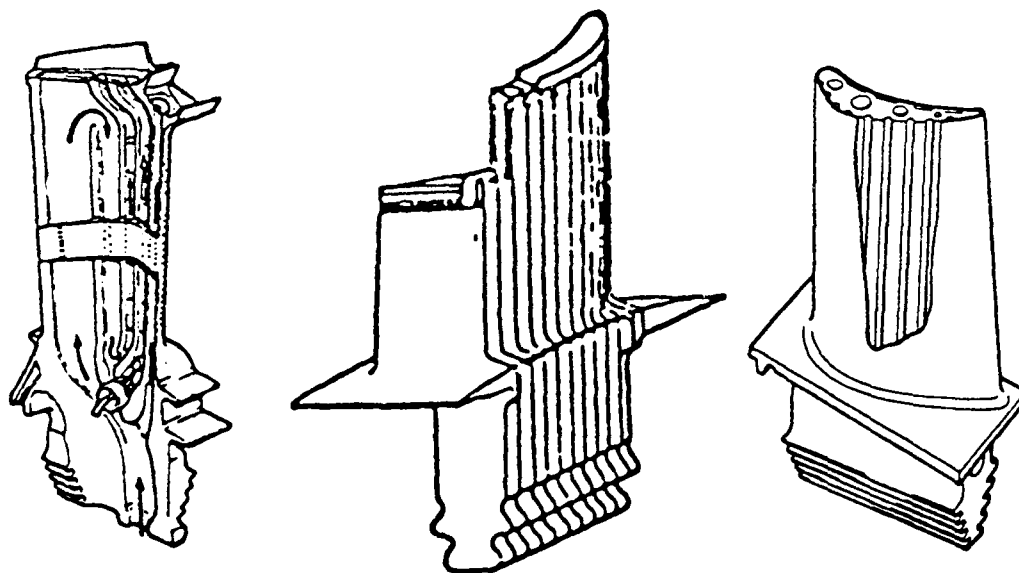


Fig 2 Cooled Turbine Blades

a) Cast Blade

b) Wafer Blade

c) Spar-shell Blade

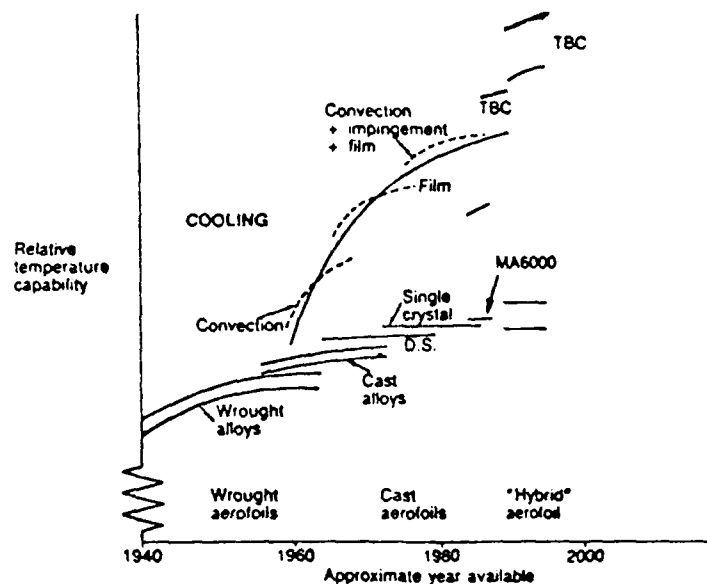


Fig 3. Combined material/cooling temperature capability.

Wafer blades incorporating RST superalloys have been proposed ⁽³⁾ and additional manufacturing steps have been further suggested to avoid the high modulus of the RST alloys. The fact that wafer blades are not in production use is evidence of the practical manufacturing problems involved and the cost effectiveness of this technically interesting technology must be somewhat dubious. The spar/shell concept introduces the possibility of multi-alloy multi-piece blades with improved cooling and material capabilities with different materials being incorporated to meet the different characteristics required in the spar and shell regions of the blade. Several realistic manufacturing routes appear possible.

The progressive improvement in temperature capability achieved by combined material, cooling and thermal barrier coating combinations is illustrated in Fig 3.

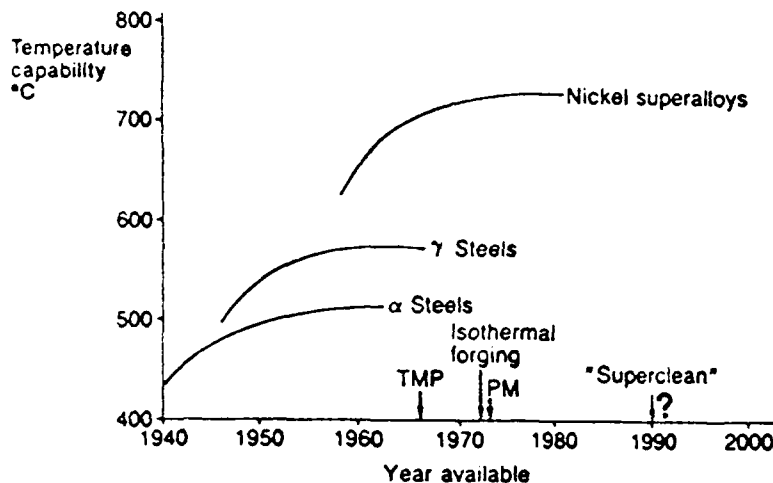
However, as shown in Fig 1, there is a large efficiency benefit to be gained from the use of still higher temperature materials which would require no cooling. Such materials would also be of benefit in small thin aerofoils in which it is difficult to manufacture an adequate cooling design. Avoidance of cooling would require increase in material temperature capability of some 300-500°C depending on blade design and the possibility of achieving this further development of nickel superalloys which are already operating with metal temperatures within 300°C of their incipient melting temperature must be somewhat limited!

3. TURBINE DISCS

Steels were used for discs in early aero gas turbine engines. They were based on the low alloy steels used for superheater tubes in steam power plant and on simple austenitic steels.

It was recognised at the time of the early gas turbines that the behaviour of discs had to be predictable and reliable since containment of a burst disc is not possible. The mechanical integrity of the steel discs in aero gas turbines was based on simple overspeed criteria which resulted in the stresses being lower than the yield stress and fatigue was essentially not a problem. It was simply considered to be a phenomenon associated with vibration and resonance which could be avoided by design.

The requirement for aero gas turbines to operate at higher stresses and temperatures led to the introduction of the nickel superalloys. When they were introduced, these alloys were so superior to steels (Fig 4) that only elementary microstructural control was required from the forging process.



- Fig 4. Disc alloy temperature capability and process developments.

During the 1960's however, it was realised that fatigue failures could occur in these materials at stress levels permitted by the overspeed criteria and that life was related to the number of aircraft flights or missions. Low cycle fatigue was thus a major life limiting feature. This motivated attempts to improve properties through the generation of specified microstructures by thermo-mechanical processing. The proof strength of Waspaloy was increased by some 40% and significant improvement was achieved in the fatigue strength of Inco 901. Control of dislocation density and distribution was shown to be an important factor in the control of component behaviour in Inco 901⁽⁴⁾. Such considerations will influence the forging of highly stressed industrial gas turbine discs in Inco 901 and 718 which can be significantly bigger than the aero gas turbine discs commonly produced in these materials.

When the significance of low cycle fatigue was realised, fatigue tests were introduced in the material specifications and the forger was required to ensure the necessary microstructural control and freedom from defects. The move towards hot die and isothermal processes reflected the microstructural control required. Component life was defined on the basis of the first visible or "engineering" crack.

The need to increase blade tip speed to further increase turbine efficiency and the consequent need to operate at still higher stress levels motivated the development of stronger alloys. Problems resulting from excessive chemical segregation in these more highly alloyed materials led to the pre-alloyed powder disc technology of the 1970's. PM alloys have significantly higher proof strength than the earlier superalloys. It was subsequently recognised however that small defects such as oxides from the melting process, which cannot be found by existing NDE technology, nucleate fatigue cracks and limit fatigue strength. At the highest stress levels the cyclic margin between first "engineering" crack and component failure severely restricts component life. These considerations required new lifing philosophy and a new approach to disc material technology.

The new lifing approach, known as "life on condition" or "retirement for cause" assumes the presence of a crack of a size just smaller than the detection limit of the inspection methods available. The crack is assumed to grow in a manner predicted by linear elastic fracture mechanics. A life to failure can be calculated and a safe proportion used to declare a service life. When this is completed, the component is inspected for surface and internal defects. On passing this reinspection procedure the component is cleared for a further life and so on until a crack is found. In this approach it is essential that appropriate data is used. It has been shown for example, that the behaviour of short cracks, which are of a size similar to the surrounding microstructural features, cannot be predicted from that of large cracks. Thus the material behavioural model must accept the microstructurally dominated quasi-cleavage nature of short crack growth of current high strength disc superalloys.

In order to allow operation at the required stress levels, a new approach has been proposed for disc material technology - the total life concept⁽⁵⁾. The first requirement is the development of a manufacturing process with the capability to avoid defects which can act as propagating cracks. Such processes have been referred to as "superclean". The second requirement is the establishment of a comprehensive understanding of short crack growth and nucleation behaviour. This is essential in designing alloys and microstructures for resistance to crack nucleation and growth and the necessary balance of strengthening mechanisms may well be somewhat different from that in current alloys. This total life concept has the potential for providing the capability of operating at the required higher stresses.

4. HIGH TEMPERATURE FABRICATED STRUCTURES

The components in this category include combustion chambers, jet pipes and reheat components. They are normally welded fabrications largely using sheet nickel superalloys. In order to achieve higher cycle temperatures it is necessary to burn more fuel and this in turn requires more primary air for combustion. This results in a reduction of the amount of air remaining for cooling the combustor walls and for reducing the temperature of the combustion gases to a level which the turbine will accept (Fig 6). The problem is compounded by pollution regulations restricting the amount of smoke and NO_x generated by both

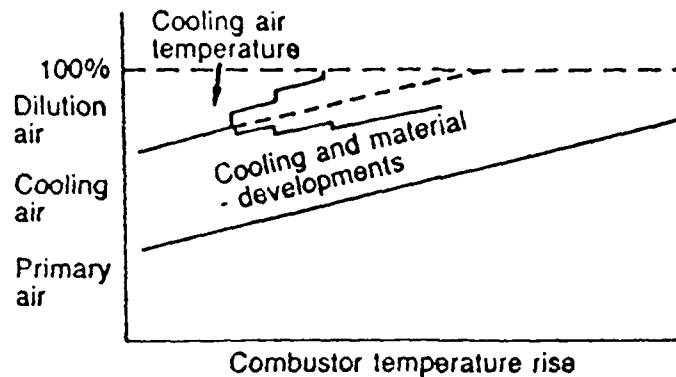


Fig 6. Requirements for increased combustor temperature rise.

aero and industrial gas turbines. Improved cooling effectiveness has been achieved by the progressive development of film cooling technology and by the use of techniques such as transpiration cooling. The benefits from such improvements however have been offset to some extent by the higher cooling air temperatures arising from increased compression ratios. Thus increased temperature capability has continued to be a major requirement for combustor materials, with restrictions being imposed to date by fabrication and weldability considerations.

A similar requirement applies to materials for reheat components, reheat providing supersonic thrust in military engines. Since the fuel is burned at relatively low pressure in the jet pipe its thermodynamic efficiency is low and thus supersonic flight duration is restricted in reheated engines. The need to improve the capability for supersonic flight can be achieved by designing for higher levels of specific thrust with higher turbine entry temperature and lower by-pass ratio. Thus future reheat components will operate in even higher temperature environments. Heat shields have normally been cooled by techniques broadly similar to those used in combustors and cooling of flameholders will also become necessary unless improved materials can be developed.

Significant improvements have already been achieved in strength and oxidation resistance of the conventional nickel superalloys used in combustor and reheat applications.

For the past decade thermal barrier coats have been standardised in some combustors. Metal temperatures have been reduced by some 50°C and this technology will be developed further.

Oxide dispersion strengthened alloys such as MA956 have the potential for operating at significantly higher metal temperatures although lack of weldability in such materials will require new fabrication techniques. Use of tiled constructions is a possibility but the increased weight of such designs may not be acceptable in military engines where thrust/weight is of prime importance. However, despite such possibilities the ultimate operating temperature environment in future military engine designs is likely to be beyond the capability of metallic materials and new types of material will be required.

5. CURRENT MATERIALS IN RELATION TO FUTURE REQUIREMENTS

Further increase in turbine entry temperature will be achieved by anticipated advances in cooling technology with nickel superalloy aerofoils. Thermal barrier coatings which insulate and provide environmental protection will also make a major contribution. However, the highest temperature requirements may be beyond the capability of this combined technology and significant increase in efficiency would be achieved if cooling could be avoided. Thus all types of gas turbines would benefit from aerofoil materials with higher temperature capability than nickel superalloys.

Turbine disc requirements in industrial gas turbines will be met by the use of materials which have been standard in aero gas turbines but the larger component sizes will require further developments in forging technology.

The aero gas turbine need for materials with higher useable strength to increase turbine efficiency has not been met by the powder disc approach but it is possible to see the way forward via the total life concept which has been discussed.

The ability of nickel superalloys to allow the combustor temperature rises required by future advanced engine designs is severely limited by the reduction in cooling air which will be available at the projected conditions and by the need for dilution air to reduce the temperature of the combustion gas to a level acceptable for the turbine. Higher temperature turbine aerofoil materials will help this situation, but this will not obviate the need for higher temperature materials for the combustor. Such materials would avoid the performance and cost penalty associated with increased air cooling of reheat components.

Thus materials with very significant higher temperature capability than nickel superalloys are required by some major engine components.

Several material systems meet this requirement but all have some inherent problem which must be overcome before they can be regarded as serious contenders. The refractory metals have been explored in the past but their inability to form protective oxides means that they are dependant on coatings for environmental resistance. The other material systems with useful temperature potential are non metallic and some, such as silicon nitride and silicon carbide have been run in demonstrator land based gas turbines. Even if the further work that is required to ensure their reliable application is successful however they will not meet the temperature requirement for all future engine designs and new material systems are required.

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The shaping of structural engineering ceramics

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ABSTRACT: The main shape-forming methods for engineering ceramics, particularly for components of complicated shape, are compared in respect to technical and economical advantages and disadvantages. Different development trends are presented.

Hot isostatic pressing using the glass encapsulation technique offers a good way to avoid nonuniform deformation during sintering which is important for complicated shapes.

Combined efforts in these areas by the Swedish companies KemaNord Industrikemi AB, ASEA Cerama AB and United Turbine AB have made possible the development of a vehicle gas turbine rotor in HIP-ed silicon nitride. Some details of the performance experience of this component are given.

1. INTRODUCTION

Engineering ceramics now begin to become an alternative to metals in areas where it is important to have a very high resistance towards wear, corrosion and elevated temperatures and often all these requirements at the same time. Typical materials are silicon nitride, silicon carbide, alumina, zirconia etc. They have found several applications and many of them are already produced commercially (table 1).

Table 1: Commercially produced engineering ceramics

- * Bearings, seals, ball bearings
- * Wear components: Various parts for paper, textile, and rubber industries; radomes, armor, sand blasting nozzles, wire-drawing dies, mills, mixers, filters
- * Bioceramics: hip prosthesis, dental implants
- * Cutting tools
- * Burner and rocket nozzles, advanced refractories
- * Heat exchangers
- * Catalyst supports
- * Heat engine components: Hot plug, prechamber, port liner, turbo charger rotor, burning chamber

The main problem, which still prevent their use as an engineering material on a larger scale in the industry is their brittleness with a low fracture toughness and probabilistic fracture strength determined by an inherent flaw population. The fracture toughness and also the reliability could be increased by different hardening mechanisms using particles or fibres/whiskers. However the most important thing both for monolithic ceramics and for the reinforced ceramics is to reduce number and size of defects such as pores, inclusions, agglomerates, cracks etc.

At our institute we think that in general the shape-forming of the components together with the raw material preparation and post-forming treatment such as dewaxing and drying, are the most critical steps in the processing of almost all ceramics. In this paper the main forming methods will be compared and special attention will be given to hot isostatic pressing. Finally some information will be given on present co-operative research in Sweden, particularly the KTT gas turbine.

2. SHAPE-FORMING TECHNIQUES FOR ENGINEERING CERAMICS

2.1 Comparison of forming methods

In table 2 are compared the main general advantages (+) and disadvantages (-) of different forming methods used for engineering ceramics. A comparison can only be made within a single row, i.e. in respect to a special issue for different forming methods, but not between different rows because the issues are not of the same importance. +/- or -/+ means an advantage or disadvantage depending on specific details. The most probable situation is mentioned first. NA means not applicable for that particular issue and forming method.

Hot isostatic pressing requires normally an additional pre-forming method that could be any of the other mentioned genuine forming methods.

It is possible to combine the genuine forming methods, for instance a slip cast or cold pressed component could be additionally compressed by cold isostatic pressing.

2.2 Trends

CP: Die pressing is still the single most important shape-forming method. The intrinsic problems of the method are tried to solved by better pressing aids, tailor-made for the specific system.

HP: Will be used primarily for R & D work. For production the HIP will be preferred.

CIP: Will be used particularly for large components or very demanding smaller ones. Small components in long series require dry-bag technique where a die is combined with a flexible mould.

Table 2: Comparison of different forming methods for engineering ceramics

	CP	HP	CIP	HIP	EXTR	IM	SC
<u>Geometry, quantity</u>							
Complex shapes	-/+	-	-/+	+	-	+	+
Large sizes	-	-	+	+	+	-	+
Small wall thickness	-	-	+	+	+	+	-
Close tolerances	+	+	-	+	+/-	+	-
Long series	+	-	-/+	+	+	+	-/+
Short series	-/+	+	+	+	-	-	+
<u>Microstructure (*)</u>							
Small and few defects	-	+	+	+	-/+	+	+
High density	+/-	+	+	+	+/-	+	+
Uniform density distr.	-	+/-	+	+	+/-	+	+
Isotropy	-	-	+	+	-	+/-	+/-
<u>Time</u>							
Short forming time	+	-	-/+	-	+	+	-/+
Short post-forming time	+	NA	+	NA	+	-	-/+
High productivity	+	-	-/+	+	+	+	-/+
<u>Cost</u>							
Low machinery cost	+	+	-	-	-	-	+
Low mould cost	-	+	+	+/-	-	-	+
Low forming aids cost	+	+	+	+	-	-	+
<u>In practice</u>							
Simplicity	+	-	+	-	-	-	+
Experience	+	+	+	-/+	-	-/+	-/+
<u>Environment</u>							
Health hazards	-	-	-	+/-	+/-	+/-	+
Emissions (pollution)	+	+	+	+	-/+	-	+

Notes

CP: (Cold) Pressing, die pressing, uniaxial pressing

HP: Hot Pressing

CIP: Cold Isostatic Pressing

HIP: Hot Isostatic Pressing not a genuine shape-forming method - requires a primary shape-forming such as pressing, injection moulding or slip casting

EXTR: Extrusion

IM: Injection Moulding

SC: Slip Casting

+: Advantage

-: Disadvantage

+/-: Advantage/Disadvantage depending on specific details

NA: Not applicable

*) Green microstructure for genuine forming methods and final microstructure after sintering for HP and HIP.

HIP: Further development to reduce cost disadvantages => improved glass encapsulation technique (more automatic, less system dependent) and sinter-HIP (post-HIP). Primary advantages with

HIP are the possibilities to obtain fully dense materials at relatively low temperatures without too much sintering aids and also the capability of near-net-shape to avoid excessive machining.

EXTR: Improvement of processing aids.

IM: Stronger competition from other forming techniques. Problems with dewaxing (long processing times, cracks) have to be solved. Development towards lower pressures => less expensive moulds; perhaps water-based systems.

SC: Today an alternative to the other more established shape-forming techniques. Further development of variants such as soluble mould casting and pressure slip casting. Wet processing is an advantage as regards health hazards and agglomeration.

However, the most important trend concerns basically the preforming step. Powder blends will be developed for different shape-forming methods incorporating all the necessary processing aids. For instance canned slips of silicon nitride will be available suitable for forming by slip casting and subsequent pressureless sintering at a specific temperature giving properties adapted for a specific application with the required reliability.

3. HOT ISOSTATIC PRESSING

Activities on hot isostatic pressing of engineering ceramics have been going on in Sweden since about 15 years. Gradually this method has developed into a powerful production technique for top quality components. Two different routes can be used:

A) The component is pre-formed by for instance injection moulding. After dewaxing the component is enclosed in a suitable cannister or encapsulated via glass powder that is melted to a dense coating by raising the temperature. Then a pressure is applied and by increasing the temperature to the top temperature a final pressure of 100-300 MPa is reached (Larker 1984).

B) The pre-formed component is first sintered by pressureless sintering (ambient pressure) to a density where no open porosity remains which usually happens at 90-95 % of the theoretical density. Then the component is post-HIP-ed without any encapsulation. The method is often called sinter-HIP.

The first route using glass encapsulation has been developed by the Swedish company ASEA Cerama AB at Robertsfors (Larker 1984). Materials like pure or low-doped Si_3N_4 , SiC , B_4C and TiB_2 can be densified at temperatures between 200°C and 500°C below what is needed when pressureless sintering is used (Hermansson et al 1986). The low sintering temperature reduces the risk of exaggerated grain-growth and unwanted reactivity in the material which is important for fiber and whisker reinforced ceramics (Lundberg 1987).

4. DEVELOPMENT OF ENGINEERING CERAMICS IN SWEDEN

Typical of the Swedish R & D activities in this field is the strong co-operation between different companies such as raw material producer - component producer - engineering industry user (table 2)

and also between the industry and universities/institutes (table 4-5.) The R & D is usually market oriented and the general philosophy from the government authorities like the Swedish National Board for Technical Development is to support basic materials science research, processing research and production engineering research.

Table 3: Industrial companies with research on high performance ceramics in Sweden.

Producers of ceramics

ASEA Cerama AB	HIP technology
ASEA Switchgear AB	varistors
Berol Kemi AB	processing additives
EKA Nobel AB	raw materials, catalysts
KemaNord Industrikemi AB	raw materials
AB Sandvik Coromant	cutting tools
AB Sandvik Hard Materials	wear parts
Seco Tools AB	cutting tools

Users of ceramics

Saab Scania AB	heat engines
SKF AB	ball bearings
AB Volvo	heat engines
Volvo Flygmotor AB	gas turbines, space applications
United Stirling AB	stirling engine
United Turbine AB	gas turbines

Table 4: University departments with research on high performance ceramics in Sweden.

Chalmers University of Technology - Göteborg

Engineering Metals	joining, fiber composites
Inorganic Chemistry	raw materials synthesis
Physics (Prof. Gordon Dunlop)	microstructure
Polymer Technology	injection moulding

Luleå University of Technology - Luleå

Materials Technology (Prof. Thomas Johansson)	machining, HIP technology, joining, reaction sintering
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Royal Institute of Technology - Stockholm

Physical Metallurgy and Ceramic Technology (Prof. David Rowcliffe)	mechanical properties, thermodynamics
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University of Stockholm - Stockholm

Inorganic Chemistry (Prof. Tommy Ekström)	raw materials synthesis, thermodynamics, micro- structure
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University of Umeå - Umeå

Inorganic Chemistry	thermodynamics
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University of Uppsala - Uppsala

Inorganic Chemistry	CVD technique
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Table 5: Industrial Research Institutes with research on high performance ceramics in Sweden.

Swedish Institute for Silicate Research (SSFI) - Gothenburg	basic processing science and technology, mechanical properties
The Institute for Surface Chemistry (YKI) - Stockholm	processing additives
The Swedish Institute of Production Engineering Research (IVF) - Luleå	HIP technology, joining
Studsvik Energy Technique - Nyköping	corrosion, erosion

As an illustration of this co-operative spirit it could be mentioned that the ASEA Cerama company is owned by the following companies with their ceramic interests indicated in brackets.

50 % ASEA (HIP-technology, ZnO-varistors, superconducting ceramics)
 10 % KemaNord (Si and Si_3N_4 raw materials)
 10 % Sandvik/Seco Tools (cutting tools, engineering ceramics)
 10 % Volvo (ceramics for heat engines)
 10 % SKF (ceramics for ball bearings)
 10 % Boliden (ceramics for wear applications)

However the total number of people involved in ceramic R & D at both companies and universities/institutes are not very great, perhaps 60 people altogether.

Government sponsored ceramics R & D in Sweden within special programs is rather small and amounts to approximately 10 MSEK/year (1 MGBP/year) with the following distribution (1986):

High performance ceramics	52 %
Inorganic binders (Portland cement)	23 %
Glasses	14 %
Traditional ceramics	8 %
Various	3 %

The government support will probably be increased this year:

Major program (5 years) on Structural Ceramics: 9 MSEK/year (1 MGBP/year).

Minor program on Electronic Ceramics: 1 MSEK/year (100 kGBP/year).

6. THE KTT GAS TURBINE ROTOR

As an example of these joint developments I will present some details on the ceramic axial gas turbine rotor produced by ASEA Cerama AB for the motor company United Turbine AB (belonging to the Volvo-group) (fig. 1).

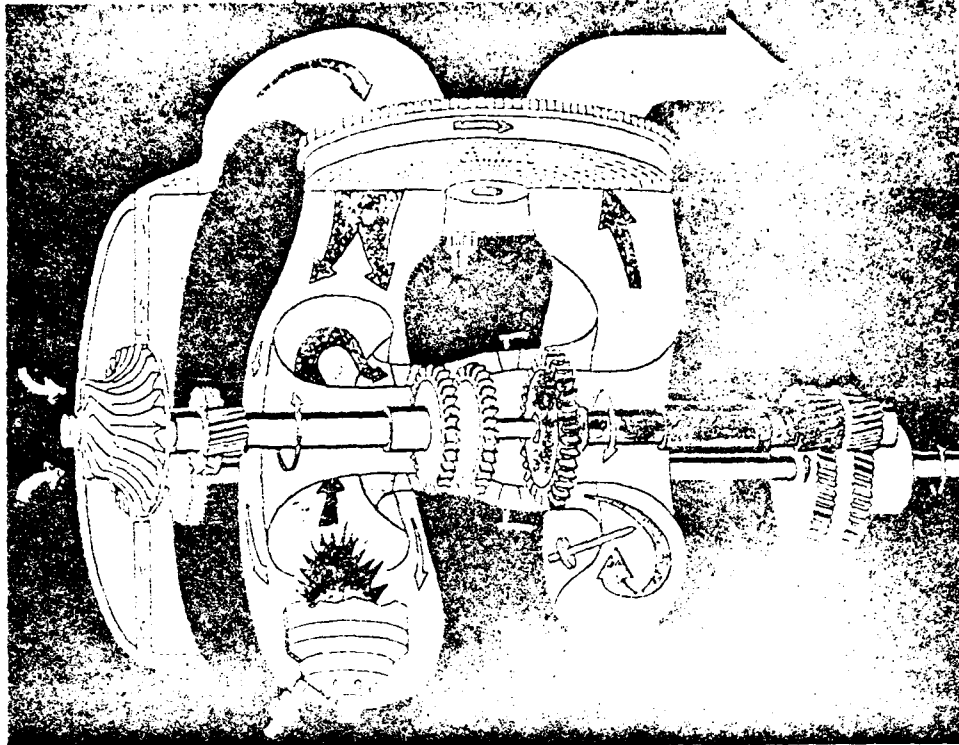


Fig. 1. Outline of the KTT gas turbine (courtesy United Turbine AB)

Table 6: Some specification for the axial KTT ceramic gas turbine rotor.

Design: Axial gas turbine rotor with aerodynamically twisted blades (fig. 2). The trailing edge of the blades is just 0.25 mm and the thickest part of the rotor is approximately 25 mm.

Material: Silicon nitride.

Maximum loss: 1 out of 100 rotors by
 a) Starting up transient
 b) Full power at a turbine inlet temperature of 1370°C which corresponds to a material temperature of 1300°C; speed 75000 rpm and 100 h. During the driving cycle the turbine rotor will be highly mechanically and thermally loaded in the temperature interval 300°C to 1250°C with maximum stresses up to 300 MPa.

Production yield: Greater than 90 %.

The vehicle gas turbine concept of United Turbine is a special 3-shaft gas turbine called KTT (Kronogård Turbine Transmission). There are four ceramic parts in this gas turbine, namely the burning chamber (in Refel SiC-Si), the rotor and the stator of the first turbine stage, and the heat exchanger (in Corning Li-Al-silicate). The turbine rotor is designed by United Turbine AB and some specifications are given in Table 6.

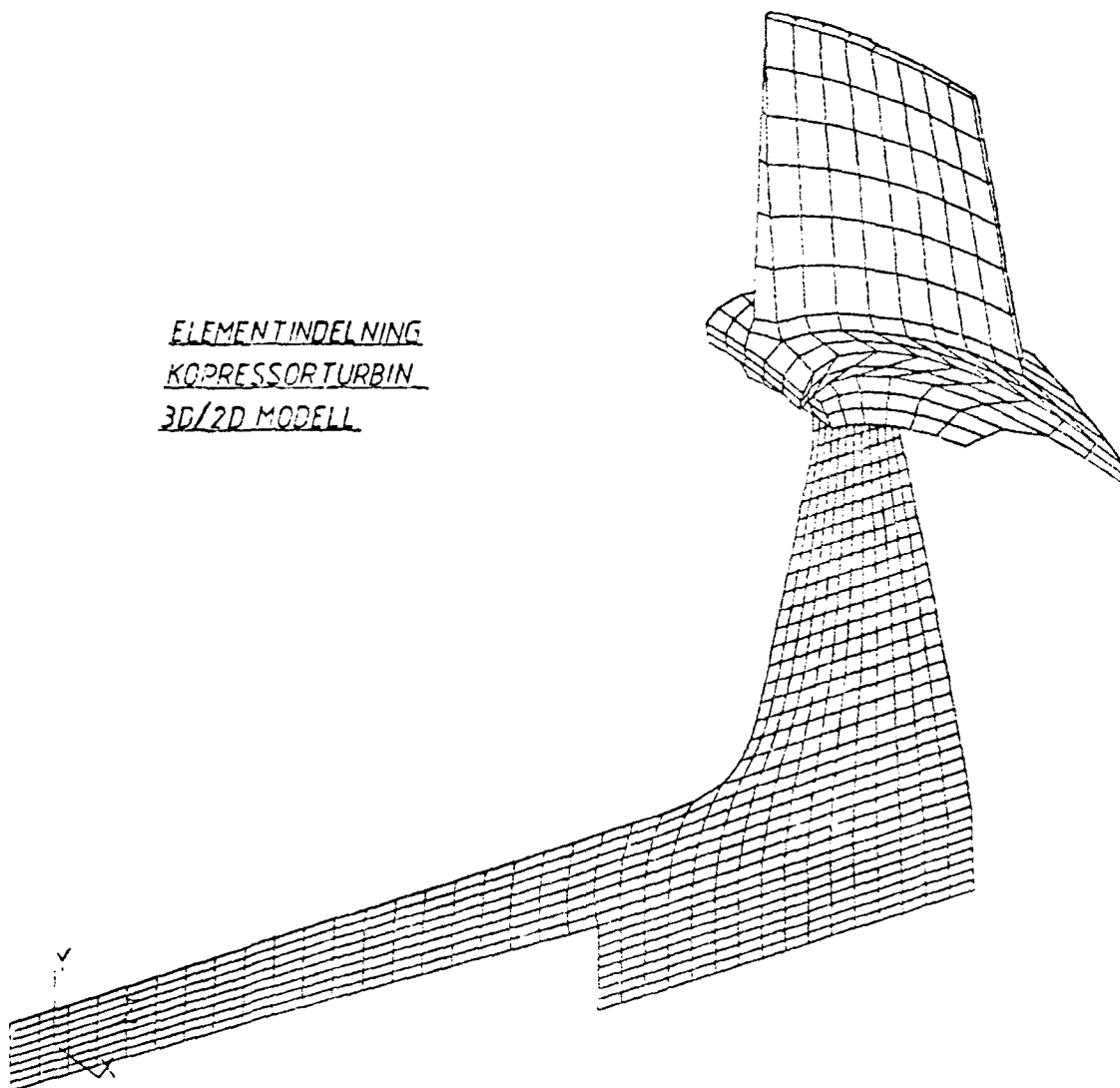


Fig. 2. Finite element division of a KTT ceramic gas turbine rotor blade (courtesy United Turbine AB)

The rotor is injection moulded in a very complicated mould (fig. 3). After dewaxing the rotor is treated at 700°C to remove all moisture and residual organic substances, glass-encapsulated and HIP-ed. The only machining after the removal of the glass encapsulation is a grinding of the stub shaft to fit the axle attachment and of the outer periphery to reduce gas losses (Hermansson et al 1986). Balancing is made by selecting the position of the shaft machining. Today the performance of this ceramic gas turbine rotor is rather close to the objectives (table 7). Test runs are made with this rotor in a KTT turbine equipped passenger car.

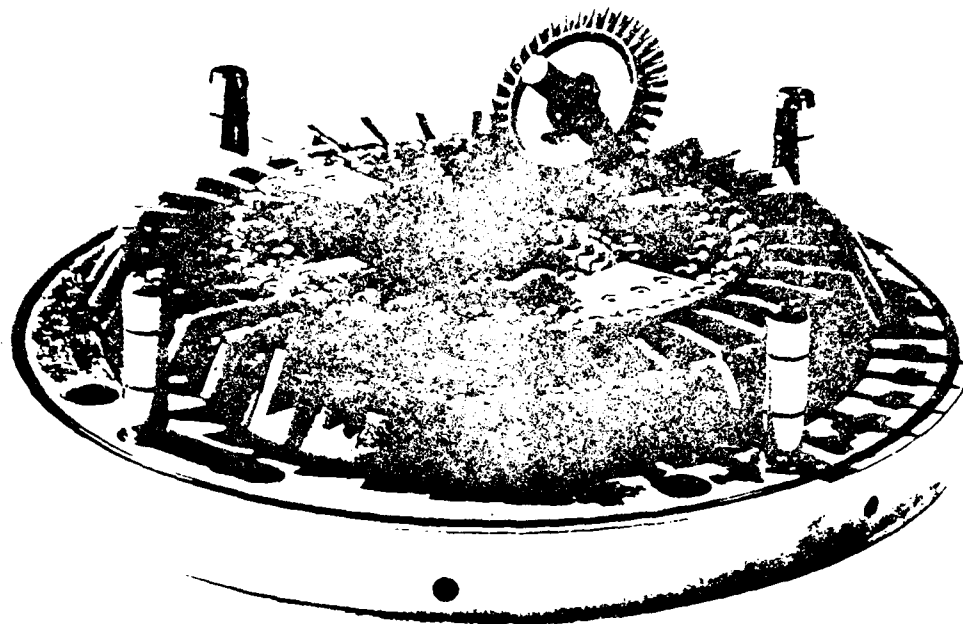


Fig. 3. Mould for injection moulding of the KTT ceramic gas turbine rotor with the glass encapsulated hot isostatically pressed rotor on top (courtesy United Turbine AB and ASEA Cerama AB)

Table 7: Performance of the axial KTT ceramic gas turbine rotor 1986

Bending strength (in component, 4-point bending, RT): 500-600 MPa

Full speed: 70000 rpm

Tip speed: 400 m/s

Weibull modulus (in component): 8-10

Temperature: Not reported

7. ACKNOWLEDGEMENT

The author wants to thank ASEA Cerama AB and United Turbine AB for their kind help with details about the development of the KTT gas turbine rotor.

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Time and Temperature Dependence of Strength in High Performance Ceramics

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ABSTRACT: A hierarchical approach to time-temperature-strength evaluation based on stepped temperature stress rupture (STSR) testing, stress rupture (SR) testing, and the development of fracture mechanism maps will be presented. Utilization of this hierarchical philosophy will be illustrated with examples of data from materials at different levels of maturity, i.e., hot-pressed silicon nitride, Y-TZP, and toughened Al_2O_3 .

1. INTRODUCTION

High performance ceramics such as the silicon nitride, silicon carbide, toughened zirconia and toughened alumina families of materials are the "enabling" materials for many advanced energy conversion technologies. Indeed, advanced diesel, gas turbines and industrial heat exchanges are either benefiting from or projected to benefit these advanced ceramics. The societal payoff in terms of energy savings from the use of high performance ceramics in these roles is large, as shown in Table I. These large fuel savings coupled with the potential for reduced maintenance resulting from reduced corrosion (of heat exchanger tubes or via elimination of engine cooling systems) represent the major driving force for the development of these ceramics.

Since the principal high temperature structural applications of advanced ceramics will demand service lifetimes ranging from several thousand to several tens of thousands of hours, the time and temperature dependence of the strength of these materials is of major concern. During the course of long duration, elevated

Table 1. PAYOFF OF STRUCTURAL CERAMICS IN SELECTED APPLICATIONS

APPLICATION	PAYOFF	MATERIALS
• LIGHT-DUTY DIESEL (UNCOOLED)	10-15% REDUCTION IN SPECIFIC FUEL CONSUMPTION	ZIRCONIAS, SILICON NITRIDES, SILICON CARBIDES, ALUMINAS, ALUMINUM TITINATES
• HEAVY-DUTY DIESEL (ADIABATIC)	22% REDUCTION IN SPECIFIC FUEL CONSUMPTION	ZIRCONIAS, SILICON NITRIDES, SILICON CARBIDES, ALUMINAS, ALUMINUM TITINATES
• LIGHT-DUTY AUTOMOTIVE GAS TURBINE	27% REDUCTION IN SPECIFIC FUEL CONSUMPTION	SILICON NITRIDES, SILICON CARBIDES, LAS, MAS
• RECUPERATOR FOR SLOT FORGING FURNACE	42% REDUCTION IN FUEL CONSUMPTION	SILICON CARBIDES

temperature service many changes can occur in a material. In the case of silicon nitrides and carbides oxidation can create new flaw populations and/or reduce the severity of initial flaws. In the case of toughened oxide ceramics such as partially stabilized zirconia, phase transformations and/or grain growth are possible. Because material changes such as these typically occur over long periods of time, the extrapolation of results obtained from short-term laboratory tests, such as dynamic fatigue or slow crack growth experiments (minutes to only several hours) can be very misleading. Therefore, in our laboratory we have come to depend almost exclusively on stress rupture tests to evaluate the time-temperature dependence of the strength of structural ceramics. Most appropriate to the topic of this workshop, we use stress rupture tests not only to generate life prediction data, but also in the development of new materials and improved materials processing procedures.

The amount, sophistication and reliability of data required in the early stages of materials development are quite different from the data needed in order to successfully design components from mature engineering ceramics. Furthermore, during the early phases of materials development it is important to have meaningful results quickly so that these can provide feedback for processing and compositional modifications. In order to best serve the various purposes to which stress rupture data are likely to be used we have evolved a hierarchical test philosophy in which each step in the hierarchy addresses a different stage of materials development. These hierarchical steps are:

- 1) Stepped Temperature Stress Rupture (STSR) testing, for screening "new" materials early in the development cycle.
- 2) Conventional Stress Rupture (SR) testing, for providing detailed characterization and life prediction data for materials which are beginning to emerge into reliable engineering materials.
- 3) Fracture Mechanism Maps, which combine long-duration SR testing of natural and artificially flawed specimens with extensive fractography to provide guidance to the mechanical designers. These maps are appropriate only in the case of established, mature engineering ceramics.

These three procedures will be discussed in some detail in the following three sections, together with some recent examples of their use.

2. THE STEPPED TEMPERATURE STRESS RUPTURE TEST

The STSR test is an extension of the common flexural stress rupture test to include a range of temperatures (Quinn & Katz, 1978). In this test a specimen is loaded into a furnace equipped with a four-point bend fixture and the furnace is heated in air to some desired temperature, T_1 . When T_1 is reached a deadweight load is applied to the sample. Should the sample survive 24 hours at that temperature, the furnace is then heated (usually 10 to 30 minutes) to the next desired temperature, T_2 , and again allowed to soak for 24 hours. Provided the sample does not fail, this cycle is repeated for as many additional temperatures as desired. Usually the temperatures are raised in 100C increments.

Throughout the test, the sample is subjected to a constant deadweight load. If a sample breaks, the furnace is cooled and unloaded and the time-of-failure is denoted by an arrow on the STSR plot. The arrow is labeled with the stress that was applied to the sample.

An arrow pointing to the left at the beginning of the test indicates an initial failure upon loading. An arrow pointing to the right at the end of the test sequence indicates a sample surviving with no failure.

Although the temperature history of a STSR specimen is more complex than that in a conventional stress rupture test, the key intention is that any unusual temperature sensitivity will be identified quickly with a minimum number of specimens. Figure 1 illustrates a "normal," well-behaved material, i.e., time-dependent failures occur at progressively lower stresses as one increases temperature and the transitions occur rather gradually as one goes from one temperature to the next. Such behavior is not always observed as will be seen in many of the examples that follow.

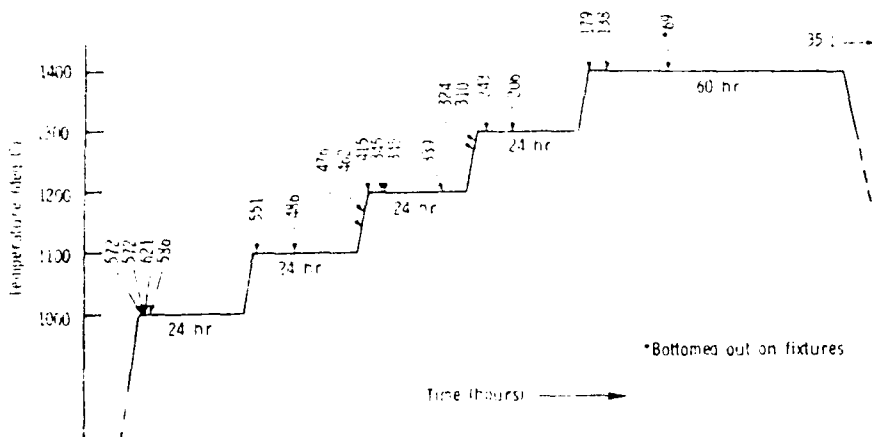


Figure 1. STEPPED TEMPERATURE STRESS RUPTURE DATA FOR NC-132 HPSN. ARROWS INDICATE FAILURE TIMES, ARROW LABELS SPECIFY STRESS ON SAMPLE IN MN/m² (ksi).

Over the past decade the STSR test has been used by our laboratory (Quinn & Slavin, 1986) to evaluate hot pressed, sintered, and reaction-bonded silicon nitrides. Hot pressed, sintered and reaction-sintered SiC's have also been extensively evaluated using the STSR method. Most recently our group at MTL has been utilizing the STSR technique to screen the time-dependent strength behavior of toughened oxides, MgO stabilized partially stabilized zirconia (Mg-PSZ) (Schioler et al, 1984), yttria stabilized tetragonal zirconia polycrystal (Y-TZP) (Swab, 1987) and SiC whisker-toughened Al₂O₃ (Tracy & Slavin, 1987).

Partially stabilized zirconia's show a significant reduction in strength when aged at elevated temperatures, therefore it is not surprising that the strength exhibited by PSZ's should degrade markedly when evaluated in the STSR test. That this is indeed the case can be seen from Figure 2 which is a typical STSR plot for a

high RT strength Y-PSZ and Figure 3 which is a typical STSR plot for a Mg-PSZ. Figure 2 indicates that toughened zirconias can exhibit "normal, well-behaved" STSR plots (in the sense described above), whereas Figure 3 illustrates a material with anomalous behavior. The anomaly here is that the time-dependent failures seem to be insensitive to temperature between 800 and 1100C.

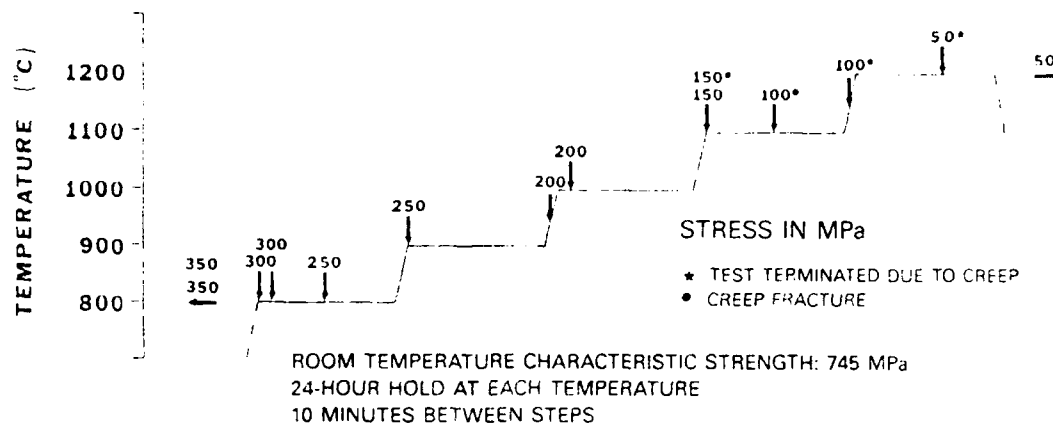


Figure 2. STSR PLOT OF A COMMERCIAL Y-PSZ.

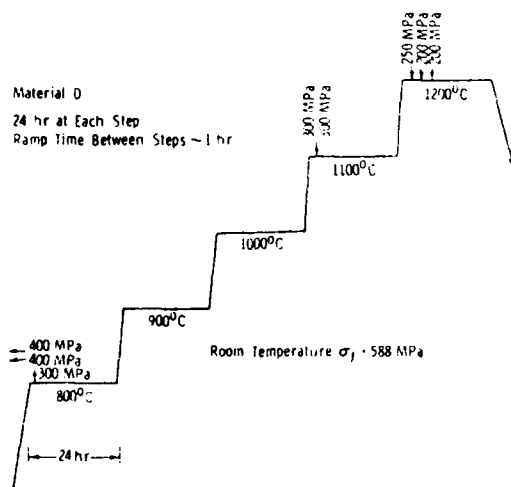


Figure 3. STSR PLOT OF A COMMERCIAL Mg-PSZ.
(Schioler, 1987)

The STSR test has recently been used to elucidate the role of slight deviations from stoichiometry on the high temperature, time-dependent strength of hot isostatically pressed (HIP'ed) Y-TZP (Swab, Katz, & Starita, 1987). In this instance a commercially available HIP'ed Y-TZP was determined to be slightly oxygen deficient in the as-received state. The STSR test was used to compare the time-temperature-strength behavior of both the as-received, slightly O₂ deficient Y-TZP, and of material which was oxidized for 100 hours at 1000C to restore stoichiometry. The results are compared in Figure 4. The oxidation treatment increased the strength by a factor of 2-3 for temperatures below the heat treatment temperature. By the time the as-received

material goes through the 24 hour, 1000C portion of the STSR test it is fully oxidized, so there is essentially no difference in the two materials beyond 1000C. The point here is that the use of the STSR procedure enabled completion of a study of the above effect over the temperature range of 800-1200C and a wide range of stresses over a period of about two months time and with only 30 test bars. Conventional SR testing over the same temperature and stress ranges would have required at least 100 test bars and six months or more. Additionally, these tests provided information on the onset and course of creep behavior. This example of the use of the STSR in materials research is also an example of the practical benefits of the technique. Since the technique is "low cost" in terms of time, specimens, and equipment, we use it as part of our routine materials evaluation. Thus, we have recently obtained some of the first data on the time-temperature-strength behavior on Al_2O_3 - SiC whisker-reinforced composites (Figure 5) even though our principal interest in this material was for a low temperature application.

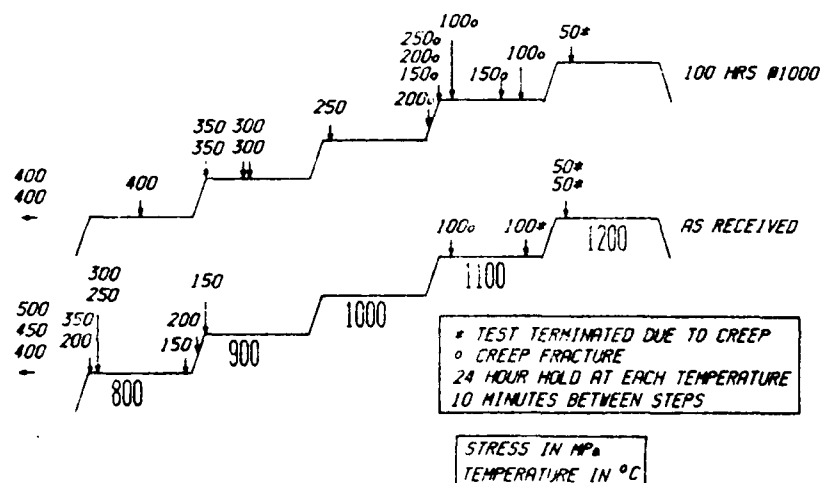


Figure 4. EFFECT OF OXIDIZING HEAT TREATMENT ON THE STRESS RUPTURE PERFORMANCE OF HIPed Y-TZP.

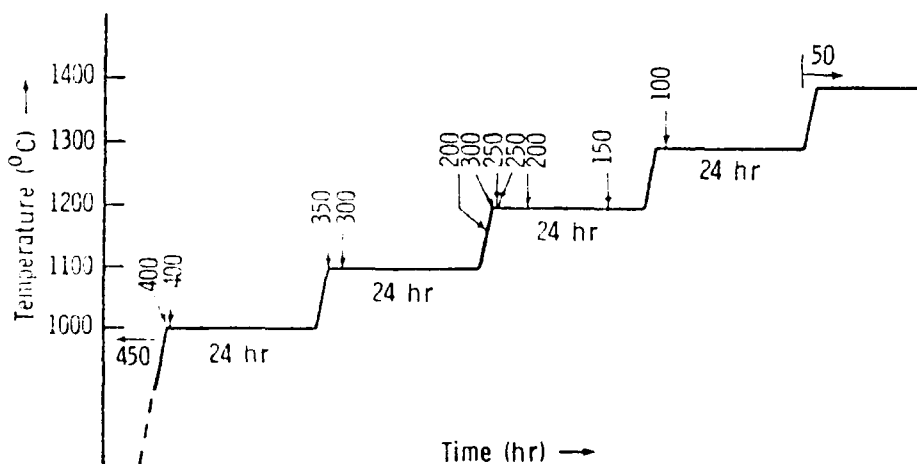


Figure 5. STSR PLOT OF Al_2O_3 MATRIX - 25 w/o SiC WHISKER COMPOSITE, TESTED IN AIR.

3. CONVENTIONAL STRESS RUPTURE TESTS

Stress rupture testing enables one to evaluate materials at temperatures, stresses, and in some cases, stressed volumes approximating those encountered in service. In addition SR tests can be used to obtain data for life prediction calculations. The reciprocal slope of the SR curve (in log-log form) is the exponent n in the slow crack growth power law:

$$V = AK^n \quad (1)$$

where: V is the crack growth rate, A is a constant, and K is the stress intensity factor. The data and the value of n obtained by these investigators are significantly more consistent than results obtained in double torsion tests or variable strain rate strength testing (Quinn & Quinn, 1983). Figure 6 (Baker et al, 1983) illustrates the wide variation in life predictions possible when using different methodologies. That the experimental observations fit the SR based life predictions is probably due to both the increased constancy of the exponent n , and to the fact that a 50-hour life prediction using SR data is an interpolation not an extrapolation.

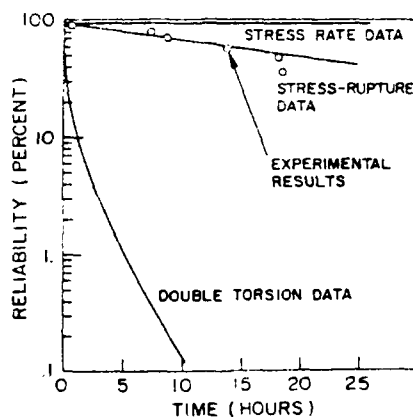


Figure 6. LIFE PREDICTION CALCULATIONS AND EXPERIMENTAL RESULTS FOR A HOT-PRESSED SILICON NITRIDE TURBINE DISK TESTED AT 50,000 rpm AND 1260°C RIM TEMPERATURE. (Baker et al., 1983)

Stress rupture data is preferred for life prediction (NMAB, 1980), yet it is very time consuming and expensive to acquire. The SR data shown in Figure 7 (Quinn, 1986) for HPSN required approximately 150 specimens and over 25,000 furnace hours. Thus, comprehensive SR studies are worthwhile only for materials which are commercially available and are well on their way to application. Therefore, it is not surprising that the most extensive SR data on structural ceramics is available for the silicon nitrides and carbides.

There are as yet essentially no SR data on toughened zirconias or aluminas. Figures 8 and 9 present a summary of SR data for various silicon nitride and silicon carbide based ceramics, respectively.

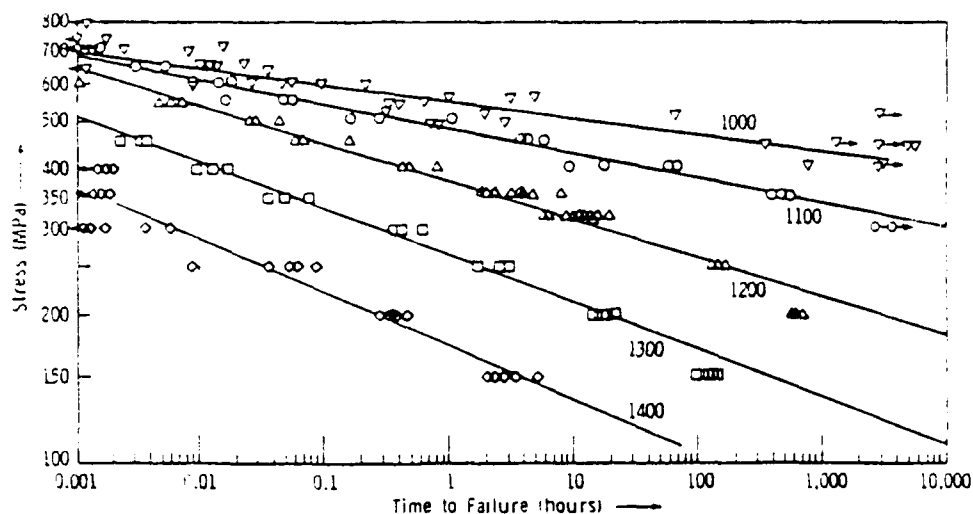


Figure 7. FLEXURAL STRESS RUPTURE IN AIR FOR HPSN TEMPERATURES IN DEGREES C. AS-MACHINED SPECIMENS.

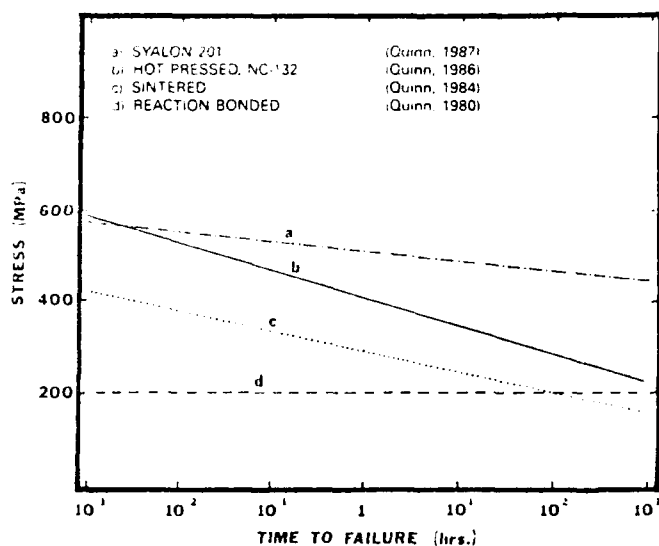


Figure 8. STRESS RUPTURE OF VARIOUS SILICON NITRIDES IN AIR AT 1200°C.

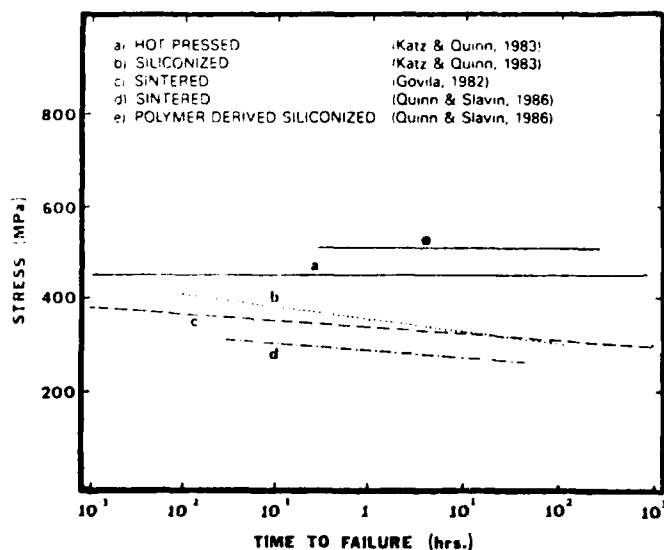


Figure 9. STRESS RUPTURE OF VARIOUS SILICON CARBIDES IN AIR AT 1200°C.

4. FRACTURE MECHANISM MAPS

Analyzing SR data such as shown in Figure 7 in order to estimate safe temperature and stress limits for a ceramic component is a relatively straightforward task for specialists in the mechanical behavior of ceramics. However, most traditionally trained design engineers do not have the experience to confidently interpret such data. Recognizing that this difficulty has been a barrier to the broader application of modern high temperature ceramics, several researchers have recognized the need for fracture mechanism maps to facilitate design (Quinn, 1986, Matsui et al, 1986). Such maps delineate the temperature and stress fields where various fracture mechanisms are dominant. These maps are generally prepared for a given design lifetime, i.e., 5000 or 10,000 hours. Matsui et al, (1986) have prepared such a fracture map using analytic models for fast fracture, slow crack growth, creep, and oxidation to be used as a basis for sintered silicon nitride turbocharger design. Quinn (1986), on the other hand, has derived a fracture mechanism map from experimental data utilizing SR data from samples with native flaw populations, plus SR results from artificially induced flaws combined with extensive fractographic analysis. Figure 10

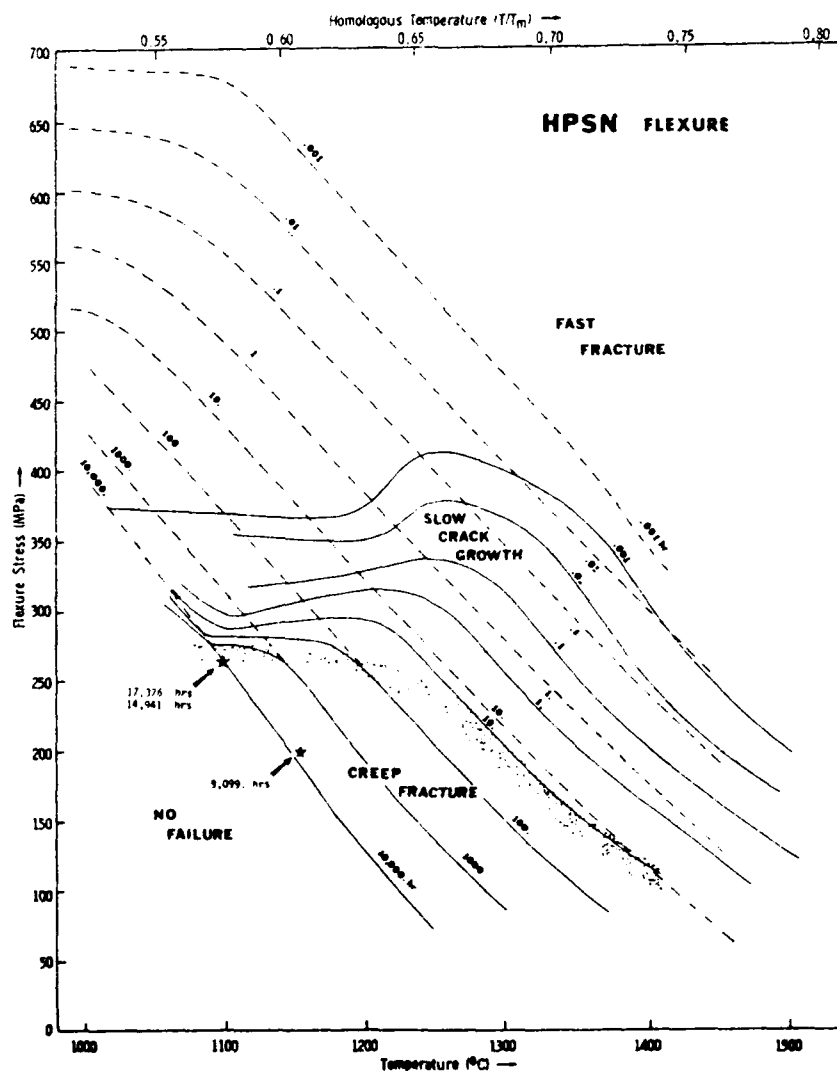


Figure 10. FRACTURE MECHANISM MAP FOR NC-132 HPSN. (QUINN, 1986)

shows Quinn's fracture mechanism map where the artificial flaw (solid lines) and as-machined (dashed line) stress rupture results replotted as constant time-to-failure loci, are both shown. Over much of the stress temperature field, slow crack growth (SCG) from preexisting flaws led to fracture. The artificially flawed specimens failed in less time than similarly loaded as-machined specimens since the much larger artificial flaw required less crack growth to failure. Thus, the dashed lines are above and to the right of the solid lines. Under some conditions the failure loci overlapped, and the artificial flaws had no effect upon time-to-failure. This is the creep fracture zone. In the creep fracture regime, failure did not occur from the artificial flaw. The SCG creep fracture zones were differentiated by observation of failure location. Three experiments utilizing artificially flawed specimens and of unusually long duration are highlighted. The 9099-hour failure did not break at the artificial flaw, but the 17,376-hour failure did. The 14,941-hour specimen exhibited creep fracture with partial involvement of the artificial flaw.

5. SUMMARY

This paper has illustrated the application of stress rupture testing in a three stage hierarchy, each stage of which is appropriate for a different level of materials development. The STSR test is well suited to the early stages of materials development. The conventional SR test is appropriate to more mature materials. The most sophisticated use of SR data, in the development of fracture mechanism maps which can facilitate the design process, is appropriate for only the most mature engineering ceramics. It is hoped that this brief review will encourage the wider use of stress rupture testing in the development of new and improved high temperature structural ceramics.

6. ACKNOWLEDGEMENT

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ABSTRACT: The developments of engineering ceramics in the Federal Republic of Germany is described by stating the objectives and considering the achievements of the three main projects sponsored by the BMFT: 1) Ceramic components for vehicular gas turbines (1974-83), 2) Follow-up of 1) with the stress on improving reproducibility and reliability and extension to other engines (1983-86), 3) High performance structural ceramics (as part of a large new programme of research on materials, 1985-94). These projects involved an increasingly close collaboration between raw-materials suppliers, component manufacturers, universities and research institutes.

1. INTRODUCTION

In the years before the war, Germany had a high reputation for its production of ceramics for electronic components and in the post-war years Degussa's AL23, a dense high-purity alumina, was used worldwide, but the year 1974 is probably the most accepted point-of-time when the Federal Republic of Germany (FRG) began research and development of engineering ceramics. At that time the BMFT (Bundesministerium für Forschung und Technologie, Federal Ministry for Research and Technology), no doubt scared by the oil crisis and encouraged by the activity in the U.S.A., initiated the first project to be jointly operated by the automotive and ceramic industry and supported by research at various institutes and universities. Its objective was to develop a ceramic gas turbine. This project ran originally for 9 years but was extended from 1983 to 1986 with a slightly modified programme. More recently the engineering ceramic activity has become a part of a much wider Materials Research Programme intended to run for ten years from 1985 to 1994.

The aims and achievements of these programmes will be detailed in this paper. This will be followed by a survey of the participating industrial companies concerned with the supply of suitable raw materials, manufacturers of the required ceramic components, and their users. Finally, the research effort supporting the industrial work will be discussed by mentioning the specific fields in which the various institutes have become eminent.

2. BMFT - SPONSORED PROJECTS

2.1 Ceramic Components for Automotive Gas Turbines (1974-83)

The choice of the gas-turbine as power unit was based on the following

advantages compared with the piston engine:

- a. saving of rare, expensive or strategically important raw materials
- b. greater acceptability from environmental point of view: lead-free fuel, lower emission of undesirable substances from exhaust, less noise
- c. saving of energy, lower fuel consumption, higher efficiency at equal volumes but lower weight, multifuel capacity

In order to achieve the above advantages a working temperature of 1350°C was required. The materials selected for development were silicon nitride and silicon carbide. Three engine manufacturers i.e. Volkswagen (VW), Daimler-Benz and Motoren-und Turbinen Union (MTU) participated in the project developing gas turbines of 100, 150 and 300 kW, respectively. The rotor represented the most difficult task. VW

and MTU were opting for a hybrid rotor i.e. ceramic blades inserted into a metallic disc, (Figure 1), whilst Daimler Benz chose an integral rotor made of hot-pressed silicon nitride (HPSN) which had to be machined from a hot-pressed disc with diamond tools (Figure 2). Because of the great expense of the production process this cannot be considered a commercial solution but in 1984 Daimler-Benz were able to demonstrate that a passenger car using a gas turbine with ceramic components (Figure 3) was capable of being driven by road from Stuttgart to Bad Neuenahr, a distance of over 200 miles. The task of producing the required ceramic components i.e. combustion chamber, nose cone, turbine scroll, nozzle guide vanes, recuperative heat exchanger and rotor blades were allocated to the following component manufacturers: Annawerk (Ceranox division), Rosenthal Technik, Sigri, Elektroschmelzwerk-Kempten, ESK and Feldmühle. These firms had to use a variety of shaping techniques to produce the above components. During the period 1974-83 the material properties were considerably improved e.g. the strength of reaction-bonded silicon nitride (RBSN) and HPSN were doubled. This was achieved in part by the development of improved starting materials by H.C. Starck.

The total expenditure during this period was 96 MDM (£32M). The government funded 50% of the industrial expenditure but 100% of the research institutes' expenditure. The breakdown can be seen in figure 4. The much larger total subsidy to industry compared with research institutes is noteworthy. The management of this project was carried out by the DFVLR (Deutsche Forschungs-und Versuch-anstalt für Luft-und Raum-fahrt, German Aerospace Research Establishment) on behalf of the BMFT. Although much had been achieved during the period 1974-83 it was clear that the economic mass-production of such parts as combustion chamber, inlet scroll, heat-exchanger, nozzle guide vanes and rotor required a great deal more

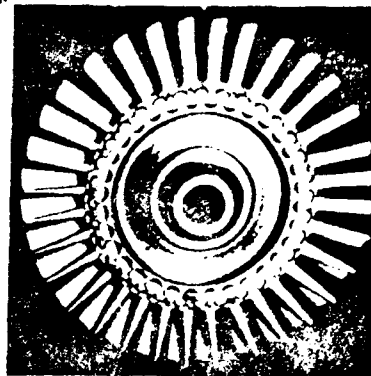


Fig. 1. Hybrid rotor

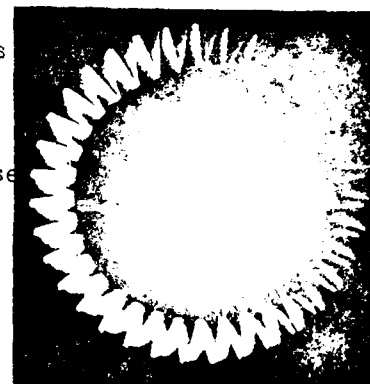


Fig. 2. Rotor under-going hot test at 1350°C



Fig. 3. Daimler Benz "car 2000"

research and development. In the absence of a very clear idea in what direction long-term future work was to go, a short-term interim project was decided upon.

2.2 Follow-up Programme (1983-86)

The project aims for this follow-up programme were slightly changed. It emphasized the need for greater reproducibility of materials properties and reliability of components. Thus it stressed the need for more work on the preparation of powders, the processing of components and their final evaluation by NDE.

To a certain extent the scope was widened by bringing in other materials e.g. zirconia, aluminium titanate, and the application of ceramic components was no longer to be limited to the gas turbine but included other applications, foremost of which was the Diesel engine. During this period a number of commercial applications of engineering ceramics were introduced e.g. the exhaust port liner by Porsche and Audi, valve seatings valve tappets and rocker arm tips. These innovations must be ascribed to an increasing familiarity of engineers with ceramic materials. However, novel applications of the new ceramic materials went beyond the field of combustion engines; they were found in metals processing, in the refractory field, in electronics and biotechnology.

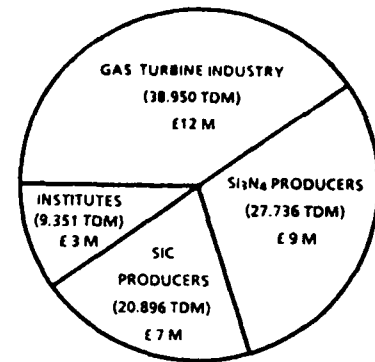


Fig. 4.

2.3 Material Research Programme (1985-94)

This programme covers all types of materials and applications in which innovation was of technical and economic significance; it aims at securing long-term industrial competitiveness. Within the total budget for the ten years, 220 MDM (£70M) have been allocated to high-performance structural ceramics. The project management which is now undertaken by KFA (Kernforschungsanlage, nuclear research centre, Jülich) encourages the formation of project groups with participants from industry and research institutes. Two or more industrial competitors may participate in one project but as far as the project is concerned they have to cover different aspects e.g. a number of powder producers may be in the same project but one may be concerned with silicon nitride, another with silicon carbide etc. In this new project the support for R & D is 50% of the total expenses including that of research institutes. These have to find therefore 50% funding either from industry, their own funds or from other non-national or international sources e.g. Volkswagen foundation. In April 1986 13 projects had been started with more than 30 partners. By today many more projects have been started or are about to start; the funds required are now close to the limits of the budget. Each programme has a review point; if as a result, it is terminated, funds become available for a new project.

The operation of these projects is illustrated by a particular example e.g. FASKER. This is the abbreviated name for "fibre-reinforced composites with ceramic matrix". FAS is derived from "FASER" which is to be interpreted to cover whiskers, short and long fibres; KER comes from Keramik which covers ceramics, glasses and glass ceramics. The objective is to develop fibre-reinforced composites, giving particular attention to the interface between the fibre and whisker-matrix and to characterize the materials by their thermo-mechanical properties. The

industrial participants are :Schott Glasswerke, Hoechst, Sigmund
Elektrographit GmbH; the research institutes: the University Karlsruhe,
the Technical University Berlin, the DFVLR and Battelle (Frankfurt). Thus
it combines the expertise of industry and research institutes in the fields
of glass, glass-ceramics, ceramics, fibre-composites (see also section 3).
This project is intended for 10 years but will be reviewed after 3 years
and a further 4 years. If it has progressed sufficiently to warrant user
interests one or more user firms with potential applications will join the
project. Another project on whisker-reinforced ceramics is about to
start, its participants are: Hüls, Haldenwanger, Maschinenfabrik Augsburg-
Nürnberg (MAN), Fraunhofer Institut, Würzburg and the Technical
University Hamburg-Harburg.

2.4 Other Programmes Involving Ceramics

These programmes fall within the following categories:

Energy: burners, heat-exchangers, two-stroke/two-cylinder engines, sodium-
sulphur storage batteries, hydrogen technology (Hot Eddy) and
Solar power (GAST).

Health: artificial joints and implants.

Transport: Ceramic components for Otto and Diesel engines (KEBOD).

Environmental Technology: catalyst carriers for exhausts.

The total funding of these projects from the federal government up to
1986 amounted to 75 MDM or £25M.

3. INDUSTRY

In this section the most important firms, their expertise and any
important recent changes will be indicated.

3.1 Ceramic Powder Producers

Bayer A.G. the large chemical and pharmaceutical firms who decided
a few years ago to enter the field of engineering ceramics. They bought
a share of the Central Research Institute of the Cremer-group who own
Annawerk and Friedrichsfeld. Thus they obtained much of the knowledge of
the Ceranox - (non-oxide ceramics) division of Annawerk which had been
sold some years earlier to Feldmühle (see below). More recently they
purchased the H.C. Starck GmbH the most successful developer of non-
oxide powders.

Dynamit Nobel producer of zirconia and aluminium titanate.

Degussa started recently experimental production of a variety of
powders.

Elektroschmelzwerk Kempten (ESK) produce most non oxide powders e.g.
silicon carbide, silicon-, aluminium-, and boron-nitride and many
borides.

W.C. Heraeus produce aluminium nitride for their own manufacturing
activity.

Lonza-Werke sinterable silicon carbide (SiC)

H.C. Starck (see also Bayer) SiC, silicon nitride (SN), AlN and other
non oxides e.g. carbides, borides.

Vereinigte Aluminium Werke AG (VAW) aluminium oxide.

3.2 Manufacturers of Ceramic Components

Annawerk developed components made of SN and SiC but sold their

Ceranox division to Feldmühle.

Didier-Werke mostly refractories but recently also engineering ceramics.

ESK (see also under powders) fabricate non-oxide components notably turbo-charger rotors by injection moulding and many other components.

Feldmühle very important producer of a great variety of components (e.g. cutting tools) in oxides and non-oxides. The latter by purchase of the Ceranox division of Annawerk.

Friedrichsfeld alumina and zirconia ceramics. They purchased the alumina production of Degussa many years ago. Part of the Cremer-group.

W.C. Heraeus components of AlN.

Hoechst CeramTec resulted from the purchase of Rosenthal-Technik.

A wide range of engineering ceramic products notably the development of a sophisticated heat exchanger.

Hutschenreuther a manufacturer of traditional table-ware but recently interested in engineering ceramics. (SiC glide rings for pump seals, and catalysts jointly with Degussa).

Krupp Widia manufacture oxide and non-oxide cutting tools.

Rosenthal Technik now Hoechst CeramTec.

Sigri engineering components from silicon-infiltrated silicon carbide and carbon.

3.3 Users of Engineering Ceramics

Audi port-liner of aluminium titanate in commercial production

Bosch automotive electric components, spark and glow plug.

Brown, Boverie & Cie high temperature engineering.

Daimler Benz gas turbine and diesel engine components.

Dornier-System "Hot-Elly" (hydrogen from water by hot electrolysis) and GAST (solar power).

Ficht 2-stroke/2 cylinder engine.

Greiner & Partner oil-less 2-stroke engines.

Kolbenschmidt pistons

Kühnle, Kopp & Kausch turbochargers.

MAN heat engines.

Motoren und Turbinen Union (MTU) aircraft gas turbines.

Porsche portliner in commercial production.

Volkswagen (VW) automotive ceramic components.

4. RESEARCH INSTITUTES

4.1 Institutes Mainly Funded By Government

Bundesanstalt für Material-Prüfung (BAM) Computerized ultrasonic testing.

Deutsche Forschungs-und Versuchsanstalt für Luft-und Raumfahrt (DFVLR)
(German Aerospace Research) Project management, research on silicon nitride and composites.

Kernforschungsanlage (nuclear research centre) Jülich KFA Proj. manage.
Max-Planck-Institut, Stuttgart Research on most aspects of ceramics and composites (Prof Petzow)

Frauenhofer-Institut, Freiburg Fracture mechanics

Frauenhofer-Institut, Saarbrücken Non-destructive testing

Frauenhofer-Institut, Würzburg Sol-gel derivatives

4.2 Private Research Institutes

Battelle, Frankfurt
Cremer-Forschungs-Institut

Composites
Now mostly working for Bayer

4.3 Universities

<u>Technische Universität, Berlin</u>	Synthesis of sinter-active
powders (Prof. Hausner), glass (Prof. Brückner)	
<u>Technische Universität, Clausthal</u>	Joining of ceramics (Prof.
Hennicke)	
<u>Technische Universität Hamburg-Harburg</u>	Composites, methods of
toughening (Prof. Claussen)	
<u>Universität Karlsruhe</u>	Materials science and
technology closely integrated with engine design and construction (Prof. Thümmeler)	

5. CONCLUSIONS

The considerable involvement of industry and research institutes, aided by substantial funding from the federal government puts the Federal Republic of Germany, together with the USA and Japan, amongst the three top-ranking countries in the development of engineering ceramics and their applications. Whilst originally the traditional ceramic industry (e.g. Rosenthal, Annawerk) showed interest in this new field, one can now perceive a move towards the big chemical/pharmaceutical industry (Hoechst, Bayer) who are more able to invest in long-term risk-ventures. Nevertheless, some traditional ceramic firms e.g. Hutschenreuter (tableware), Didier (refractories) have decided not to be by-passed by the new developments. The early involvement of the automotive industry through the gas-turbine project has created a degree of familiarity of their engineers with engineering ceramics so that these new materials will be considered seriously in the future, subject, of course to the criteria of cost and reliability.

6. GENERAL REFERENCES

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